Interlaboratory research on factors affecting the calibration of electrodes used for sediment sulfide analyses at fish farms

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by

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ABSTRACT

Chang, B.D., Lewis-McCrea, L.M., Wong, D.K.H., MacKeigan, K.G., Page, F.H., Cameron, S.L., Sweeney, R.H., and Smith, A.E. 2014. Interlaboratory research on factors affecting the calibration of electrodes used for sediment sulfide analyses at fish farms. Can. Tech. Rep. Fish. Aquat. Sci. 3090: v + 66 p.

Sediment sulfide concentration is the key indicator used to evaluate the impacts of benthic organic enrichment under marine salmon farms in New Brunswick, Nova Scotia, and British Columbia. Some differences in the Standard Operating Practices or Procedures (SOPs) for sediment sulfide measurement exist among the provinces, and these may contribute to variability in results. This project examined some factors that could affect the accuracy of the calibration of electrodes used to measure sediment sulfide concentrations, focussing on factors which vary among the different SOPs. Research was conducted at two labs: Sweeney International Marine Corp. (SIMC, Halifax, NS) and the St. Andrews Biological Station (SABS, Fisheries and Oceans Canada, St. Andrews, NB). In all experiments, measurements were taken in prepared water solutions with known sulfide concentrations. The choice of electrode filling solution (Orion Optimum Results A vs. B) did not have a significant effect, except at the very lowest sulfide concentrations. Comparison of calibration using 5 vs. 3 standards indicated differences between labs: at SIMC 3-point calibration produced better results, largely due to some low value outliers in the 5-point replicates, while at SABS there were no differences between the two treatments; however, confidence limits will be much narrower with 5-point calibration. Calibration using standards prepared from standardized stock solution (concentration determined by titration) produced better results than calibration using non-standardized stock solution (concentration determined by calculation). Standard solutions degraded significantly over time, with higher percentage losses in lower concentration solutions. Electrodes lost accuracy over time, with the highest rate of loss during the first few hours; the mean percentage loss over time was similar among test solutions with different sulfide concentrations (17-23% after 96 h).

RÉSUMÉ

Chang, B.D., Lewis-McCrea, L.M., Wong, D.K.H., MacKeigan, K.G., Page, F.H., Cameron, S.L., Sweeney, R.H., and Smith, A.E. 2014. Interlaboratory research on factors affecting the calibration of electrodes used for sediment sulfide analyses at fish farms. Can. Tech. Rep. Fish. Aquat. Sci. 3090: v + 66 p.

La concentration de sulfures dans les sédiments est l'indicateur clé utilisé pour évaluer les incidences de l'enrichissement organique benthique sous les exploitations salmonicoles marines au Nouveau-Brunswick, en Nouvelle-Écosse et en Colombie-Britannique. Certaines différences existent dans les pratiques d'exploitation normalisées de la mesure du sulfure dans les sédiments à l'échelle des provinces et ces différences peuvent entraîner des résultats variables. Ce projet traite de certains facteurs qui peuvent avoir une incidence sur la précision de l'étalonnage des électrodes utilisés pour mesurer les concentrations de sulfures dans les sédiments, en mettant l'accent sur les facteurs qui varient pour ce qui est des différentes pratiques d'exploitation normalisées. La recherche a été menée à deux laboratoires : le Sweeney International Marine Corp. (à Halifax, en Nouvelle-Écosse) et la Station biologique de St. Andrews de Pêches et Océans Canada (à St. Andrews, au Nouveau-Brunswick). Dans le cadre de toutes les expériences, les mesures ont été prises à l'aide de solutions d'eau préparées avec des concentrations de sulfures connues. Le choix de la solution de remplissage de l'électrode (A par rapport à B) n'a pas eu une incidence importante, à l'exception de la concentration la plus faible de sulfures. La comparaison de l'étalonnage à l'aide de la norme en cinq points et de la norme en trois points révèle des différences entre les laboratoires : au Sweeney International Marine Corp., l'étalonnage en trois points a donné des résultats supérieurs, principalement en raison de certaines valeurs aberrantes faibles pour les réplicats en cinq points. À la Station biologique de St. Andrews, les deux traitements ne présentaient pas de différence; cependant, les limites de confiance seront beaucoup plus étroites pour l'étalonnage en cinq points. L'étalonnage à l'aide des normes préparées à partir de la solution de réserve normalisée (concentration déterminée selon le titrage) offre des résultats supérieurs à ceux de la l'étalonnage à l'aide d'une solution de réserve non normalisée (concentration déterminée selon un calcul). Les solutions standard se sont beaucoup dégradées au fil du temps et présentent un pourcentage plus élevé de perte pour ce qui est des solutions à faible concentration. Les électrodes perdent leur caractère précis au fil du temps et le taux le plus élevé de perte est enregistré au cours des premières heures; le pourcentage moyen de perte au fil du temps était semblable pour les solutions de mise à l'essai comptant des concentrations de sulfures différentes (17-23% après 96 h).

INTRODUCTION

Sulfide is the key indicator currently used to evaluate organic enrichment at New Brunswick (NB) and Nova Scotia (NS) fish farms when determining their classification relative to the marine environmental quality objective of maintaining oxic conditions (NBDELG 2012a, 2012b; NSDFA 2011a, 2011b). The sulfide analytical methods used are based on research by Wildish et al. (1999, 2004). Analyses conducted on monitoring results and research data indicate that there can often be wide variations in sulfide concentrations measured at the same farm, and even among triplicate subsamples taken at the same location (Chang et al. 2011, 2013a, 2013b). It has also been found that there can be wide variations in sulfide concentrations measured at the same locations at one or two week intervals (Page et al. 2011). While such variability may indicate real small-scale spatial and temporal variation in sulfide concentrations in marine sediments, Brooks & Mahnken (2003) reported that subtle differences in protocols and/or techniques can cause significant differences in sulfide results.

Provincial government departments in NB and NS have developed Standard Operating Practices or Procedures (SOPs) for sulfide monitoring at fish farms (NBDELG 2012b; NSDFA 2011b). Similar SOPs are used for soft-bottom sites in British Columbia (BC), where environmental management of aquaculture is under the jurisdiction of Fisheries and Oceans Canada (DFO 2012). Comparisons indicate that there are some differences in the SOPs among the provinces (Table 1). To ensure that the use of sulfide in environmental monitoring of the finfish aquaculture industry in Canada is as consistent, reliable and accurate as possible, it is essential to standardize procedures.

The purpose of this project was to investigate whether some of the observed variability in sulfide results could be due to variations in monitoring methods. This one-year project has concentrated on laboratory techniques used in measuring sulfide concentrations. The initial goal is to develop a standard methodology for sulfide electrode calibration and use. It is hoped that future projects will examine other aspects of the monitoring procedures, including sample collection, transport, and storage.

Research was conducted at two labs: Sweeney International Marine Corp. (SIMC, Halifax, NS) and the St. Andrews Biological Station (SABS, St. Andrews, NB). All trials used Thermo Scientific Orion model 9616BNWP silver/sulfide electrodes (the most commonly used electrode for sediment sulfide analyses) connected to Accumet AP125 portable pH/ORP/ion meters.

The aspects of sulfide measurements that were examined in this project were:

1) *Comparison of electrode filling solutions: Orion Optimum Results A vs. Orion Optimum Results B*

There are two filling solutions that can be used with the model 9616BNWP silver/sulfide electrode to measure sulfide concentration: Orion Optimum Results B is recommended in NB

and NS, while Orion Optimum Results A is recommended in BC. Optimum Results B filling solution is supplied with the electrode and can be used for most sulfide or silver measurements and titrations; it is designed to reduce junction potentials and minimize sulfide or silver ion contamination of the sample (Thermo Scientific Inc. 2007). Optimum Results A filling solution is recommended for precise sulfide measurements; it will minimize junction potentials and provide optimum temperature and time response when sample temperatures vary (Thermo Scientific Inc. 2007). In this study, we compared sulfide measurements in test solutions with known sulfide concentrations using electrodes prepared with each filling solution.

2) Number of calibration standards: 5 vs. 3-point

NB and BC recommend using 3 sodium sulfide calibration standards: in NB, the 3 standard concentrations are 100, 1 000, and 10 000 µM; in BC, the 3 standard concentrations are 10, 100, and 1 000 µM, or 100, 1 000, and 10 000 µM (depending on the expected sulfide concentrations). NS recommends using 5 calibration standards: 100, 500, 1 000, 5 000, and 10 000 µM. In this study, we compared sulfide measurements in test solutions with known sulfide concentrations using electrodes calibrated using 5 standards (as in NS) vs. 3 standards (as in NB).

3) Standardized vs. non-standardized calibration

Calibration standards are prepared by dilution of a sodium sulfide ($Na_2S{\cdot}9H_2O$) stock solution. The sulfide concentration of the stock solution can be derived in two ways:

- Standardized: concentration determined via titration with lead perchlorate.
- Non-standardized: concentration mathematically calculated from the weight of sodium sulfide used and the volume of diluent water.

None of the SOPs specify the use of standardized vs. non-standardized calibration. However, the electrode manual (Fisher Scientific Inc. 2007) recommends that titration (i.e. standardized calibration) should be used. $Na_2S{\cdot}9H_2O$ is hygroscopic and thus absorbs water; therefore the amount weighed will be artificially high if the chemical has absorbed water over time when weighed. In this study, we compared sulfide measurements in test solutions with known sulfide concentrations using electrodes calibrated using standardized vs. non-standardized solutions.

4) Degradation of standard solutions (storage times of standards)

The length of time that sulfide standard solutions can be stored has implications for the practicality of conducting sulfide analyses in the lab vs. in the field. The BC SOPs specify that 10 000 µM standard solutions must be used within 48 h, while 1 000 and 100 µM (micromole) standards must be used within 3 h; the NB and NS SOPs do not indicate maximum storage times for sulfide standard solutions. In this study, sulfide concentrations were measured in test standards with known sulfide concentrations at 0-96 h after preparation of the solutions.

5) Electrode accuracy post-calibration (electrode drift)

In NB, electrodes can be used up to 72 h post-calibration, while in NS and BC, electrodes must be used within 3 h after calibration. In this study, sulfide concentrations were measured in freshly prepared test solutions with known sulfide concentrations at 0-96 h after electrode calibration.

METHODS

All experiments were conducted at two labs: SIMC (Halifax, NS) and SABS (St. Andrews, NB). The two labs used the same electrode model (Thermo Scientific Orion silver/sulfide electrode model 9616BNWP; see Thermo Scientific Inc. 2007), and meter model (Accumet AP125; see Fisher Scientific 2009), and similar methods. The SIMC lab used 9 meters and 10 electrodes (previously used and new). SABS used 3 meters and 3 electrodes (all new).

The number of replicate trials per experiment and the calibration standards and test solutions used in each experiment are summarized in Table 2. Appendix A includes details on the experimental chemicals and equipment; the preparation of $Na_2S{\cdot}9H_2O$ stock solutions, calibration standards, and test solutions; the preparation and calibration of electrodes; and the methods used to conduct tests. Nominal concentrations of test solutions were derived by dilution of titrated stock solution.

1) Comparison of electrode filling solutions

In each trial, one electrode was filled with Optimum Results A filling solution and a second electrode filled with Optimum Results B. Both electrodes were calibrated using 5 sulfide standards (100, 500, 1 000, 5 000, and 10 000 µM. Both electrodes were then used to measure the sulfide concentration in 4 test solutions with sulfide concentrations of 250, 750, 2 500, and 7 500 µM. Six replicate trials were conducted at each lab.

2) Number of calibration standards: 5 vs. 3-point

All electrodes were filled with Optimum Results B filling solution. In each trial, one electrode was calibrated using 5 sulfide standards (100, 500, 1 000, 5 000, and 10 000 µM) and a second electrode was calibrated using 3 sulfide standards (100, 1 000, and 10 000 µM). Both electrodes were used to measure the sulfide concentration in 4 test solutions with sulfide concentrations of 250, 750, 2 500, and 7 500 µM. Twelve replicate trials were conducted at each lab.

3) Standardized vs. non-standardized calibration

All electrodes were filled with Optimum Results B filling solution. In each trial, one electrode was calibrated using sulfide standards (100, 500, 1 000, 5 000, and 10 000 µM) prepared from a stock standard whose concentration was determined by titration and a second electrode was calibrated using standards prepared from a stock standard whose concentration was

mathematically calculated from the weight of $Na_2S \cdot 9H_2O$ and the volume of diluent water. Both electrodes were used to measure the sulfide concentration in 4 test solutions with sulfide concentrations of 250, 750, 2 500, and 7 500 µM. Six replicate trials were conducted at each lab.

4) Degradation of standard solutions

All electrodes were filled with Optimum Results B filling solution. In each trial, one electrode was calibrated immediately prior to the trial using 5 sulfide standards (100, 500, 1 000, 5 000, and 10 000 µM) and then used to measure sulfide concentrations in 7 test standards (100, 500, 1 000, 5 000, 10 000, 20 000, and 30 000 µM). Measurements were repeated at 24, 48, 72, and 96 h after preparation of the test standards; all test standards were stored in a refrigerator until the time of measurement. Electrodes were recalibrated at each measurement time. Six replicate trials were conducted at each lab.

5) Electrode accuracy post-calibration

All electrodes were filled with Optimum Results B filling solution and calibrated using 5 sulfide standards (100, 500, 1 000, 5 000, and 10 000 µM). In each trial, one electrode was used to measure sulfide concentrations in 5 test solutions (100, 500, 1 000, 5 000, and 10 000 µM) at 0, 1, 2, 3, 4, 12, 24, 48, 72, and 96 h after electrode calibration. Test solutions were freshly prepared: fresh stock solution was prepared at 0, 24, 48, 72, and 96 h; titrations were done at 0, 2, 4, 12, 24, 48, 72, and 96 h. Six replicate trials were conducted at each lab. Most trials (all at SIMC and all but the first two trials at SABS) also included control electrodes which were recalibrated at each test time (except at 1 and 3 h in SABS trials).

RESULTS AND DISCUSSION

1) Comparison of electrode filling solutions

Variability among replicates was higher at SIMC than at SABS (Table 3 and Fig. 1). Variability within each lab increased as the test concentration increased. Log_{10}-transformation resulted in similar variance among the test concentrations (Fig. 2). Analysis of variance (of log_{10}-transformed data) indicated no significant differences, except at the lowest test concentration (250 µM), where both the lab and the filling solution had significant effects (Table 4). Significant differences between measured and nominal concentrations were found only at the 250 µM test concentration at the SABS trials with filling solution B (Table 5). Appendix B includes a list of meter/electrode combinations used, and complete calibration and test data.

The results suggest that either filling solution can be used, although measurements were slightly more accurate and less variable with Optimum Results A filling solution.

2) Number of calibration standards: 5 vs. 3-point

Variability among replicates was higher at SIMC than at SABS (Table 6 and Fig. 3). Variability within each lab increased as the test concentration increased. Log_{10}-transformation resulted in similar variance among the test concentrations (Fig. 4). Analysis of variance (of log_{10}-transformed data) indicated significant differences at 3 of 4 test concentrations between labs and between the number of calibration standards (Table 7). In the SABS trials, significant differences between measurements and nominal concentrations were found only at the 250 µM test concentration with 5-point calibration. In the SIMC trials, significant differences between measurements and nominal concentrations were found at all except the lowest test concentration with 5-point calibration, but at none of the test concentrations with 3-point calibration (Table 8); however, the 5-point calibration data were influenced by a few outliers with low values. Appendix C includes a list of meter/electrode combinations used, and complete calibration and test data.

At SIMC, measurements using 3-point calibration were more accurate than measurements using 5-point calibration, which was contrary to expectations; as noted above, the results with 5-point calibration were influenced by a few outliers with low values. At SABS, measurements using both 5 and 3-point calibration gave accurate results (except at the lowest test concentration). While these results might suggest that 3-point calibration may be better than, or at least as good as, the 5-point calibration, the latter would produce much narrower confidence limits, especially at higher sulfide concentrations (confidence limit data are not included in this report).

3) Standardized vs. non-standardized calibration

Variability among replicates for standardized calibration was higher at SIMC than at SABS, but there was no consistent difference in variability between labs for non-standardized calibration (Table 9 and Fig. 5). Variability within each lab increased as the test concentration increased. Log_{10}-transformation resulted in similar variance among the test concentrations (Fig. 6). Analysis of variance (of log_{10}-transformed data) indicated no significant differences for lab effects at any of the test concentrations, but significant effects of standardization vs. non-standardization at all except the lowest test concentration (Table 10). Overall, the standardized method produced more accurate results. Using the non-standardized calibration method, significant differences between measurements and nominal concentrations were found for 3 of the test concentrations at SABS and all 4 test concentrations at SIMC. Using the standardized calibration method, there were no significant differences between measurements and nominal concentrations at any of the test concentrations at both labs (Table 11). Appendix D includes a list of meter/electrode combinations used, and complete calibration and test data.

The results indicate that standardized calibration (using titration to determine the sulfide concentration in the stock solution) produces better results; this is the calibration method recommended in the electrode manual (Thermo Fisher Scientific Inc. 2007).

4) Degradation of standard solutions

Because of calibration problems during one trial, there were only 5 replicates at SABS for the 72 h readings for 10 000 – 30 000 µM test standards. Test standards >10 000 µM were outside of the calibration range, so results for these test standards may be unreliable.

Variability among replicates was usually higher at SIMC than at SABS (Table 12 and Fig. 7). Within each measurement time, there was increased variability with increased sulfide concentration in test standards (at both labs). Within each test standard solution, the variability generally increased over time at SIMC, but not for most test standards at SABS. The mean rate of degradation was faster at SIMC for test standards 5 000-30 000 µM, but faster at SABS for test standards 100-1 000 µM.

The results indicate that there can be significant degradation within 24 h, with degradation continuing as time progressed (Table 12 and Fig. 7). The percentage loss over time (relative to the initial concentration) varied widely among test standards, ranging from 21-95% after 96 h (Fig. 8). The largest percentage losses were in the lower concentration test standards (100-1 000 µM). Wildish et al. (2004) also noted that the instability of sulfide standards is greater in weaker concentration standards. Appendix E includes a list of meter/electrode combinations used, and complete calibration and test data.

These results suggest that sulfide measurements should not be conducted using lower concentration standards that have been prepared more than a few hours before analyses are conducted. This has implications for analyses completed in the field using pre-prepared standards.

5) Electrode accuracy post-calibration

Variability among replicates in control electrodes was similar between labs, but variability was usually higher at SIMC for experimental electrodes (Table 13 and Fig. 9). Within each measurement time, there was increased variability with increased sulfide concentration in test standards, for both control and experimental electrodes. Within each test standard, there were no clear trends in variability over time in control and experimental electrodes at both labs.

At all test concentrations, measurements decreased over time with the experimental electrodes, while measurements with the control electrodes remained similar to the nominal concentrations at all times (Table 13 and Fig. 9a & 9b). The rate of decline in the experimental electrodes was highest in the first 4 h, but continued (at a lower rate of decline) throughout the trials. The percentage loss over time (relative to the initial concentrations) was similar among the test solutions; after 96 h the mean loss ranged from 17-23% (Fig. 10). Appendix F includes a list of meter/electrode combinations used, and complete calibration and test data.

SUMMARY AND CONCLUSIONS

Summary of findings:

- Variability among replicates: higher at SIMC than at SABS in all experiments.
- Comparison of sulfide electrode filling solutions: both filling solutions produced similar and accurate results.
- Number of calibration standards (5 vs. 3-point calibration standards): no significant effects in SABS trials; at SIMC, 3-point calibration produced better results, largely due to some low value outliers in the 5-point trials.
- Comparison of standardized calibration (concentration of stock solution determined by titration) vs. non-standardized calibration (concentration of stock solution determined by calculation): standardized calibration produced more accurate results.
- Degradation of standard solutions: standard solutions showed significant degradation over time, with the percentage decrease higher for lower concentration standards.
- Electrode accuracy post-calibration: electrode accuracy decreased over time, with the highest rate of decrease in the first few hours post-calibration; the mean percentage loss was similar for test solutions with different sulfide concentrations (17-23% after 96 h).

Methods were generally identical between the two labs, however, there were some differences, which may have contributed to some of the differences in results between the labs. One difference was that SIMC used crystalline sodium sulfide with a larger granular size than that used by SABS. For this reason, SIMC had to first pulverize the sodium sulfide before dissolving it in water, while this step was not required at SABS.

Another difference in methods was that SIMC used several electrodes, some previously used and some new, while SABS used only three electrodes (two in most experiments), all new. This likely contributed to the higher variability in results among SIMC replicates. The BC protocols state that routinely used electrodes should be replaced every 2 years as they become less accurate over time due to wear and tear (DFO 2012).

Sulfide is the key regulatory indicator currently used to evaluate organic enrichment at fish farms in NS and NB. Therefore, it is necessary to ensure that the methodology used for measuring sulfide concentration produces the most accurate and consistent results possible. The results from this study have contributed to clarifying some issues related to methodology. However, other questions remain, and it is hoped to continue this research to include additional work on laboratory protocols, as well as to examine issues related to sediment sample collection, transport, storage, handling, and analysis.

As noted by Wildish et al. (2004), another independent approach is needed to support the sulfide measurements. However, it can take several years to develop, test, and implement another indicator for a regulatory monitoring program.

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Table 1. Comparison of Standard Operating Procedures for sulfide measurements for monitoring sediment conditions at finfish farms in three provinces.

	New Brunswick[1]	**Nova Scotia**[2]	**British Columbia**[3]
Meter	Accumet AP63 meter or comparable	Accumet AP63 meter or comparable	Any mV meter compatible with electrode
Electrode	Thermo Orion silver/sulfide electrode (model 9616)	Thermo Orion silver/sulfide electrode (model 9616) or comparable	Thermo Orion silver/sulfide electrode (model 9616) or comparable
Electrode filling solution	Orion Optimum Results B	Orion Optimum Results B	Orion Optimum Results A
Calibration standard concentrations	100, 1 000 & 10 000 µM	100, 500, 1 000, 5 000 & 10 000 µM	10, 100 & 1 000 µM or 100, 1 000 & 10 000 µM
Storage times of calibration standards	Not specified	Not specified	10 000 µM: max. 48 h 1 000 & 100 µM: max. 3 h
Length of time electrode can be used after calibration	<72 h post-calibration	<3 h post-calibration	<3 h post-calibration
Frequency of calibration	Maximum use of 3 h	Maximum use of 3 h	Before each sampling session and every ≤3 h
Calibration check	Not specified	Not specified	Meter slope between -27 and -33
Meter check	Not specified	Plot mV and µM results from sulfide samples on the calibration curve	Not specified
Drift check	Not specified	Not specified	If electrode potentials do not stabilize in 1-2 min, measure sulfides in a dilute standard; drift deviations of 10-20% are acceptable
Sample storage	<72 h	<72 h	Begin analysis within 5 min after completion of physical analysis
Sediment sulfide readings	µM	mV and µM	µM

[1] New Brunswick Department of Environment & Local Government (NBDELG) (2012b)
[2] Nova Scotia Department of Fisheries & Aquaculture (NSDFA) (2011b)
[3] Fisheries and Oceans Canada (DFO) (2012)

Table 2. Number of replicate trials, with the calibration and test standard concentrations used in each experiment. Trials were conducted at two labs: SIMC and SABS. The number of trials shows the number of replicates at each lab.

Experiment	No. of trials	Calibration standard sulfide concentrations (µM)	Test solution sulfide concentrations (µM)
Comparison of electrode filling solutions	6+6	100, 500, 1 000, 5 000, 10 000	250, 750, 2 500, 7 500
Number of calibration standards	12+12	100, 500, 1 000, 5 000, 10 000 or 100, 1 000, 10 000	250, 750, 2 500, 7 500
Standardized vs. non-standardized calibration	6+6	100, 500, 1 000, 5 000, 10 000	250, 750, 2 500, 7 500
Degradation of standards	6+6	100, 500, 1 000, 5 000, 10 000	100, 500, 1 000, 5 000, 10 000, 20 000, 30 000
Electrode accuracy post-calibration	6+6	100, 500, 1 000, 5 000, 10 000	100, 500, 1 000, 5 000, 10 000

Table 3. Comparison of electrode filling solutions: summary table comparing measurements of 4 sulfide test solutions using electrodes prepared with 2 filling solutions (Orion Optimum Results A and B). Numbers are arithmetic means ± standard errors of measured sulfide concentrations in 6 replicate trials at each lab (12 replicate trials for the combined data).

Lab	Filling Solution	Sulfide concentration (µM) 250	750	2 500	7 500
SIMC	A	261 ± 4.8	756 ± 15.2	2 457 ± 57.9	7 457 ± 100.0
SIMC	B	253 ± 5.9	733 ± 22.4	2 342 ± 86.7	6 980 ± 273.2
SABS	A	252 ± 3.1	746 ± 4.4	2 472 ± 22.7	7 385 ± 146.8
SABS	B	240 ± 1.6	733 ± 10.5	2 472 ± 60.2	7 360 ± 216.1
Combined	A	257 ± 3.0	751 ± 7.7	2 464 ± 29.7	7 421 ± 85.4
Combined	B	246 ± 3.5	733 ± 11.8	2 407 ± 54.0	7 170 ± 175.7

Table 4. Comparison of electrode filling solutions: analysis of variance (2-factor with replication) probabilities for $\log_{10}$-transformed data. Four test sulfide solutions were measured using electrodes prepared with 2 filling solutions (Orion Optimum Results A and B), 6 replicate trials at each lab (SIMC and SABS). Probabilities in bold italics are significant ($p<0.05$).

Nominal sulfide concentration (µM)	Source of variation Lab	Filling solution	Interaction
250	***0.02***	***0.02***	0.65
750	0.76	0.22	0.73
2 500	0.23	0.33	0.35
7 500	0.42	0.19	0.25

Table 5. Comparison of electrode filling solutions: probabilities in comparisons of measured sulfide concentrations with nominal concentrations. Four test sulfide solutions were measured using electrodes prepared with 2 filling solutions (Orion Optimum Results A and B), 6 replicate trials at each lab (SIMC and SABS). Probabilities were determined using the one-sample t-test (2-tail) on $\log_{10}$-transformed data. Probabilities in bold italics are significant ($p<0.05$).

Nominal sulfide concentration (µM)	Filling solution A SIMC	SABS	Filling Solution B SIMC	SABS
250	0.07	0.53	0.72	***<0.01***
750	0.73	0.38	0.46	0.15
2 500	0.46	0.26	0.13	0.61
7 500	0.66	0.44	0.11	0.51

Table 6. Number of calibration standards: summary table comparing measurements of 4 test sulfide solutions using electrodes calibrated with 5 vs. 3 standards. Numbers are arithmetic means ± standard errors of sulfide concentrations in 12 replicate trials at each lab (24 replicate trials for the combined data).

Lab	Number of calibration standards	Test solution sulfide concentration (µM)			
		250	750	2 500	7 500
SIMC	5	229 ± 11.2	672 ± 21.0	2 146 ± 71.0	6 478 ± 245.3
SIMC	3	246 ± 6.5	736 ± 20.2	2 439 ± 86.9	7 158 ± 203.8
SABS	5	241 ± 3.5	740 ± 8.3	2 484 ± 19.6	7 543 ± 86.0
SABS	3	254 ± 5.2	765 ± 11.7	2 513 ± 34.2	7 550 ± 151.0
Combined	5	235 ± 5.8	706 ± 13.2	2 315 ± 50.4	7 011 ± 168.8
Combined	3	250 ± 4.2	751 ± 11.8	2 476 ± 46.3	7 354 ± 130.6

Table 7. Number of calibration standards: analysis of variance (2-factor with replication) probabilities for $\log_{10}$-transformed data. Four test sulfide solutions were measured using electrodes calibrated with 5 vs. 3 standards, 12 replicate trials at each lab (SIMC and SABS). Probabilities in bold italics are significant ($p<0.05$).

Nominal sulfide concentration (µM)	Source of variation		
	Lab	Number of standards	Interaction
250	0.15	***0.04***	0.67
750	***<0.01***	***<0.01***	0.20
2 500	***<0.01***	***<0.01***	***0.03***
7 500	***<0.01***	0.06	0.06

Table 8. Number of calibration standards: probabilities in comparisons of measured sulfide concentrations with nominal concentrations. Sulfide concentrations were measured using electrodes calibrated with 5 vs. 3 standards, 12 replicate trials at each lab (SIMC and SABS). Probabilities were determined using the one-sample t-test (2-tail) on $\log_{10}$-transformed data. Probabilities in bold italics are significant ($p<0.05$).

Nominal sulfide concentration (µM)	5-point calibration		3-point calibration	
	SIMC	SABS	SIMC	SABS
250	0.07	***0.02***	0.46	0.55
750	***<0.01***	0.25	0.43	0.22
2 500	***<0.01***	0.24	0.40	0.75
7 500	***<0.01***	0.67	0.10	0.82

Table 9. Standardized vs. non-standardized calibration: summary table comparing measurements of 4 test sulfide solutions. Numbers are arithmetic means ± standard errors of sulfide concentrations in 6 replicate trials at each lab (12 replicate trials for the combined data).

Lab	Calibration Method	Test solution sulfide concentration (µM)			
		250	750	2 500	7 500
SIMC	Standardized	259 ± 19.4	705 ± 36.9	2 303 ± 109.6	7 167 ± 252.3
SIMC	Non-standardized	273 ± 6.3	808 ± 8.3	2 648 ± 22.4	8 208 ± 327.4
SABS	Standardized	242 ± 3.1	731 ± 9.6	2 477 ± 37.1	7 495 ± 131.7
SABS	Non-standardized	262 ± 6.9	799 ± 11.0	2 693 ± 47.7	8 210 ± 207.3
Combined	Standardized	251 ± 9.7	718 ± 18.6	2 390 ± 61.1	7 331 ± 144.4
Combined	Non-standardized	267 ± 4.7	803 ± 6.7	2 671 ± 26.0	8 209 ± 184.8

Table 10. Standardized vs. non-standardized calibration: analysis of variance (2-factor with replication) probabilities for $\log_{10}$-transformed measurements of 4 test sulfide solutions, 6 replicate trials at each lab (SIMC and SABS). Probabilities in bold italics are significant ($p<0.05$).

Nominal sulfide concentration (µM)	Source of variation		
	Lab	Standardized vs. non-standardized	Interaction
250	0.26	0.10	0.85
750	0.58	***<0.01***	0.36
2 500	0.10	***<0.01***	0.27
7 500	0.44	***<0.01***	0.48

Table 11. Standardized vs. non-standardized calibration: probabilities in comparisons of measured sulfide concentrations with nominal concentrations. Sulfide concentrations were measured in 4 test solutions, 6 replicate trials at each lab (SIMC and SABS). Probabilities were determined using the one-sample t-test (2-tail) on $\log_{10}$-transformed data. Probabilities in bold italics are significant ($p<0.05$).

Nominal sulfide concentration (µM)	Standardized		Non-standardized	
	SIMC	SABS	SIMC	SABS
250	0.76	0.05	***0.02***	0.14
750	0.25	0.10	***<0.01***	***<0.01***
2 500	0.13	0.53	***<0.01***	***<0.01***
7 500	0.24	0.94	***0.04***	***0.02***

Table 12. Degradation of sulfide standard solutions: summary table of sulfide measurements of 7 test standards following storage times of 0-96 h. Numbers are arithmetic means ± standard errors of sulfide concentrations in 6 replicate trials at each lab (12 replicate trials for the combined data), except 5 replicates at SABS at 72 h for 10 000 – 30 000 µM.

Nominal sulfide concentration (µM)	Storage time of standards (h)				
	0	24	48	72	96
SIMC					
100	100 ± 2.5	86 ± 1.5	81 ± 4.6	73 ± 6.6	60 ± 8.6
500	489 ± 13.7	372 ± 5.4	325 ± 6.2	284 ± 13.9	242 ± 20.1
1 000	948 ± 15.3	706 ± 10.2	662 ± 26.0	610 ± 32.1	521 ± 44.0
5 000	4 735 ± 90.7	4 303 ± 143.9	3 888 ± 190.0	3 568 ± 191.1	3 297 ± 134.9
10 000	9 925 ± 333.4	8 463 ± 293.1	7 948 ± 491.1	7 910 ± 609.6	7 000 ± 407.0
20 000	19 717 ± 386.8	18 135 ± 618.8	17 233 ± 723.7	16 833 ± 866.7	16 583 ± 1 078
30 000	30 133 ± 613.6	27 467 ± 563.7	28 583 ± 1 787	26 567 ± 1 983	25 933 ± 2 283
SABS					
100	94 ± 1.7	63 ± 2.2	38 ± 6.0	37 ± 3.1	19 ± 5.4
500	476 ± 4.1	304 ± 16.9	223 ± 20.6	162 ± 29.8	102 ± 24.4
1 000	959 ± 13.0	647 ± 8.5	590 ± 12.0	504 ± 13.0	402 ± 5.0
5 000	4 790 ± 59.9	4 298 ± 54.3	4 163 ± 74.3	4 297 ± 45.4	4 028 ± 47.9
10 000	9 657 ± 72.1	9 035 ± 133.8	8 913 ± 128.0	9 144 ± 92.3	8 633 ± 103.4
20 000	19 500 ± 233.8	19 100 ± 350.2	18 267 ± 380.1	19 320 ± 156.5	18 367 ± 194.4
30 000	29 617 ± 421.4	28 983 ± 451.2	28 000 ± 482.4	29 480 ± 301.9	28 250 ± 227.7
Combined					
100	97 ± 1.7	74 ± 3.7	59 ± 7.4	55 ± 6.5	40 ± 7.8
500	482 ± 7.1	338 ± 13.3	274 ± 18.5	223 ± 24.2	172 ± 26.0
1 000	953 ± 9.7	676 ± 10.8	626 ± 17.5	557 ± 23.0	462 ± 27.7
5 000	4 763 ± 52.5	4 301 ± 73.3	4 026 ± 105.7	3 933 ± 144.3	3 663 ± 129.7
10 000	9 791 ± 167.6	8 749 ± 176.1	8 431 ± 282.3	8 471 ± 359.5	7 817 ± 317.3
20 000	19 608 ± 217.9	18 618 ± 368.9	17 750 ± 419.7	17 964 ± 577.3	17 475 ± 587.3
30 000	29 875 ± 363.3	28 225 ± 413.3	28 292 ± 887.0	27 891 ± 1 093	27 092 ± 1 148

Table 13a. Electrode accuracy post-calibration: summary table of measurements of 5 test sulfide solutions, at 0-96 h after calibration of sulfide electrodes, in trials conducted at the SIMC lab. Control electrodes were recalibrated prior to each measurement time. Experimental electrodes were calibrated prior to the first measurement (0 h) only. Numbers are arithmetic means ± standard errors of sulfide concentrations in 6 replicate trials.

SIMC	Test solution sulfide concentration (µM)					
Time (h)	100		500		1 000	
	Control	Exp.	Control	Exp.	Control	Exp.
0	103 ± 3.1	104 ± 2.9	490 ± 8.1	496 ± 13.3	976 ± 21.5	993 ± 11.5
1	102 ± 1.9	102 ± 1.2	488 ± 7.4	477 ± 11.0	965 ± 17.8	984 ± 14.6
2	101 ± 2.2	99 ± 3.1	491 ± 8.3	490 ± 18.2	988 ± 26.4	962 ± 22.9
3	105 ± 4.2	97 ± 2.5	492 ± 10.2	475 ± 9.0	981 ± 23.5	945 ± 13.4
4	100 ± 3.5	91 ± 4.9	493 ± 11.2	461 ± 18.3	990 ± 19.8	909 ± 21.5
12	104 ± 2.9	90 ± 3.2	500 ± 9.3	453 ± 17.2	983 ± 18.1	878 ± 41.4
24	103 ± 5.1	91 ± 2.3	489 ± 14.4	445 ± 10.3	963 ± 15.1	874 ± 14.1
48	105 ± 3.8	85 ± 3.8	492 ± 5.6	427 ± 16.8	966 ± 6.3	839 ± 31.8
72	104 ± 2.0	84 ± 2.7	500 ± 10.5	422 ± 9.2	998 ± 24.5	817 ± 25.0
96	102 ± 2.1	83 ± 3.8	490 ± 8.0	413 ± 12.8	966 ± 9.5	813 ± 21.3

SIMC	Test solution sulfide concentration (µM)			
Time (h)	5 000		10 000	
	Control	Exp.	Control	Exp.
0	4 885 ± 83.0	4 943 ± 98.2	9 488 ± 454.8	10 087 ± 305.0
1	4 893 ± 143.7	4 817 ± 157.0	9 820 ± 203.8	9 953 ± 306.1
2	4 958 ± 112.5	4 717 ± 122.0	9 883 ± 132.6	9 658 ± 400.2
3	5 027 ± 83.9	4 582 ± 69.8	10 120 ± 195.3	9 462 ± 201.8
4	5 067 ± 105.8	4 520 ± 87.4	10 075 ± 198.6	9 150 ± 189.3
12	4 873 ± 73.6	4 373 ± 223.3	9 942 ± 221.6	8 978 ± 599.2
24	4 808 ± 70.5	4 252 ± 95.8	9 717 ± 196.1	8 430 ± 352.0
48	4 907 ± 58.7	4 005 ± 177.6	10 040 ± 408.3	7 673 ± 476.4
72	4 925 ± 131.3	3 945 ± 169.1	10 102 ± 342.3	7 715 ± 593.7
96	4 803 ± 93.0	3 892 ± 174.0	10 358 ± 236.3	7 757 ± 602.3

Table 13b. Electrode accuracy post-calibration: summary table of measurements of 5 test sulfide solutions at 0-96 h after calibration of sulfide electrodes, in trials conducted at the SABS lab. Control electrodes were recalibrated prior to each measurement time, except at 1 and 3 h. Experimental electrodes were calibrated prior to the first measurement (0 h) only. Numbers are arithmetic means ± standard errors of sulfide concentrations in 4 replicate trials for controls and 6 replicate trials for experimental electrodes (there were no controls in the first two trials).

SABS	Test solution sulfide concentration (µM)					
Time (h)	100		500		1 000	
	Control	Exp.	Control	Exp.	Control	Exp.
0	104 ± 2.6	103 ± 1.4	501 ± 8.9	504 ± 4.6	973 ± 23.7	991 ± 9.9
1	111 ± 6.9	101 ± 1.7	495 ± 4.3	494 ± 4.6	949 ± 9.2	975 ± 10.0
2	111 ± 4.7	98 ± 1.2	517 ± 18.5	493 ± 3.5	960 ± 27.3	964 ± 6.2
3	102 ± 4.1	93 ± 3.0	479 ± 11.3	479 ± 4.5	949 ± 18.3	943 ± 10.9
4	101 ± 1.0	97 ± 2.4	485 ± 8.6	487 ± 4.4	967 ± 20.4	958 ± 9.3
12	106 ± 3.5	93 ± 0.9	499 ± 4.6	466 ± 5.1	990 ± 9.2	909 ± 9.6
24	101 ± 1.4	87 ± 3.1	490 ± 1.7	447 ± 11.6	995 ± 13.8	882 ± 20.8
48	105 ± 1.8	89 ± 1.9	497 ± 8.5	443 ± 5.9	987 ± 22.1	862 ± 14.5
72	108 ± 4.0	81 ± 4.2	514 ± 6.0	413 ± 18.0	1 005 ± 13.0	802 ± 31.4
96	103 ± 1.2	81 ± 2.2	495 ± 9.2	408 ± 9.3	1 004 ± 19.6	807 ± 15.7

SABS	Test solution sulfide concentration (µM)			
Time (h)	5 000		10 000	
	Control	Exp.	Control	Exp.
0	4 793 ± 128.5	4 957 ± 41.0	9 478 ± 384.0	9 902 ± 80.3
1	5 003 ± 385.9	4 843 ± 33.9	9 315 ± 199.2	9 922 ± 96.9
2	4 730 ± 113.5	4 852 ± 47.1	9 408 ± 162.8	9 803 ± 110.9
3	4 680 ± 96.4	4 717 ± 86.5	9 190 ± 264.0	9 590 ± 130.1
4	4 675 ± 130.2	4 823 ± 65.8	9 118 ± 427.6	9 625 ± 111.7
12	4 848 ± 54.4	4 488 ± 103.3	9 600 ± 163.2	8 882 ± 196.7
24	4 890 ± 109.2	4 508 ± 127.4	9 583 ± 273.4	8 993 ± 252.2
48	4 778 ± 120.9	4 278 ± 90.2	9 388 ± 247.6	8 653 ± 183.1
72	5 013 ± 101.4	3 995 ± 185.5	9 878 ± 292.4	8 308 ± 366.5
96	4 808 ± 136.2	4 035 ± 109.6	9 725 ± 246.4	7 977 ± 248.6

Table 13c. Electrode accuracy post-calibration: summary table of measurements of 5 test sulfide solutions at 0-96 h after calibration of sulfide electrodes, in trials conducted at the SIMC and SABS labs, combined data. Control electrodes were recalibrated prior to each measurement time, except at 1 and 3 h at SABS. Experimental electrodes were calibrated prior to the first measurement (0 h) only. Numbers are arithmetic means ± standard errors of sulfide concentrations in 10 replicate trials for controls and 12 replicate trials for experimental electrodes.

Combined Data	**Test solution sulfide concentration (µM)**					
	100		**500**		**1 000**	
Time (h)	Control	Exp.	Control	Exp.	Control	Exp.
0	103 ± 2.0	104 ± 1.5	494 ± 6.0	500 ± 6.8	974 ± 15.1	992 ± 7.2
1	105 ± 3.1	99 ± 2.0	491 ± 4.7	485 ± 6.2	958 ± 11.2	971 ± 13.7
2	105 ± 2.7	98 ± 1.6	502 ± 9.3	491 ± 8.8	977 ± 18.8	963 ± 11.3
3	103 ± 2.9	95 ± 2.0	487 ± 7.5	477 ± 4.8	968 ± 15.9	944 ± 8.3
4	101 ± 2.0	94 ± 2.8	490 ± 7.3	474 ± 9.8	981 ± 14.2	933 ± 13.4
12	105 ± 2.1	92 ± 1.7	499 ± 5.8	460 ± 8.8	986 ± 11.1	893 ± 20.8
24	102 ± 3.0	89 ± 1.9	490 ± 8.3	446 ± 7.4	976 ± 11.3	878 ± 12.0
48	105 ± 2.3	87 ± 2.1	494 ± 4.6	435 ± 8.8	974 ± 9.5	851 ± 17.0
72	105 ± 1.9	83 ± 2.4	505 ± 6.8	417 ± 9.7	1 001 ± 15.0	809 ± 19.3
96	102 ± 1.3	82 ± 2.1	492 ± 5.8	410 ± 7.6	981 ± 11.0	810 ± 12.7

Combined data	**Test solution sulfide concentration (µM)**			
	5 000		**10 000**	
Time (h)	Control	Exp.	Control	Exp.
0	4 848 ± 68.8	4 950 ± 50.8	9 484 ± 291.7	9 994 ± 152.9
1	4 937 ± 164.5	4 830 ± 76.7	9 618 ± 161.1	9 938 ± 153.2
2	4 867 ± 85.6	4 784 ± 65.6	9 693 ± 124.2	9 731 ± 199.2
3	4 888 ± 82.4	4 649 ± 56.8	9 748 ± 212.3	9 526 ± 116.1
4	4 910 ± 100.4	4 672 ± 69.4	9 692 ± 249.0	9 388 ± 126.9
12	4 863 ± 47.1	4 431 ± 118.6	9 805 ± 151.8	8 930 ± 301.0
24	4 841 ± 58.5	4 380 ± 85.3	9 663 ± 152.5	8 712 ± 223.2
48	4 855 ± 59.5	4 142 ± 103.5	9 779 ± 274.1	8 163 ± 284.7
72	4 960 ± 85.6	3 970 ± 119.9	10 012 ± 227.6	8 012 ± 344.5
96	4 805 ± 73.2	3 963 ± 100.4	10 105 ± 193.4	7 867 ± 312.4

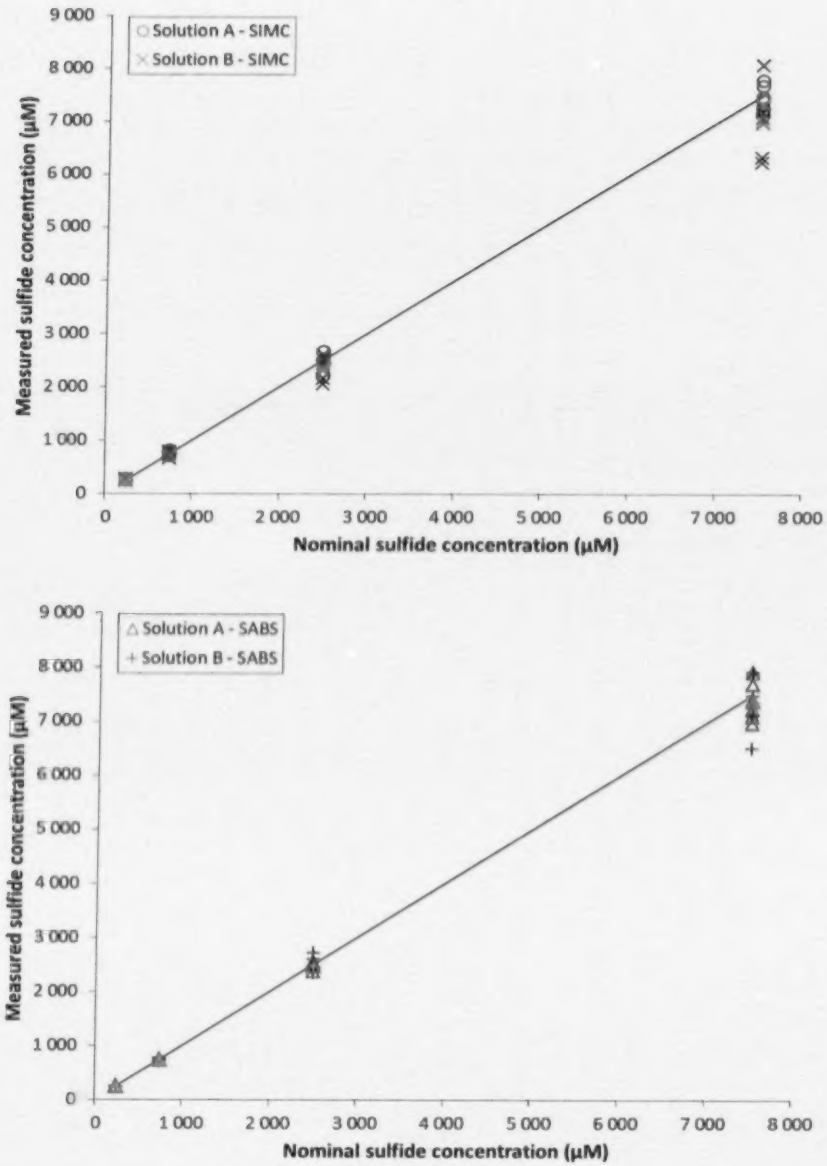
Solution A - SIMC
Solution B - SIMC
Measured sulfide concentration (µM)
Nominal sulfide concentration (µM)
Solution A - SABS
Solution B - SABS
Measured sulfide concentration (µM)
Nominal sulfide concentration (µM)

Fig. 1. Comparison of electrode filling solutions: nominal vs. measured sulfide concentrations in test solutions measured with Thermo Orion silver/sulfide electrodes using Orion Optimum Results A and B filling solutions. Experiments were conducted at 2 labs (SIMC and SABS), 6 replicate trials per lab. Top: SIMC results. Bottom: SABS results. The lines represent 1:1 ratios. Red symbols are mean values.

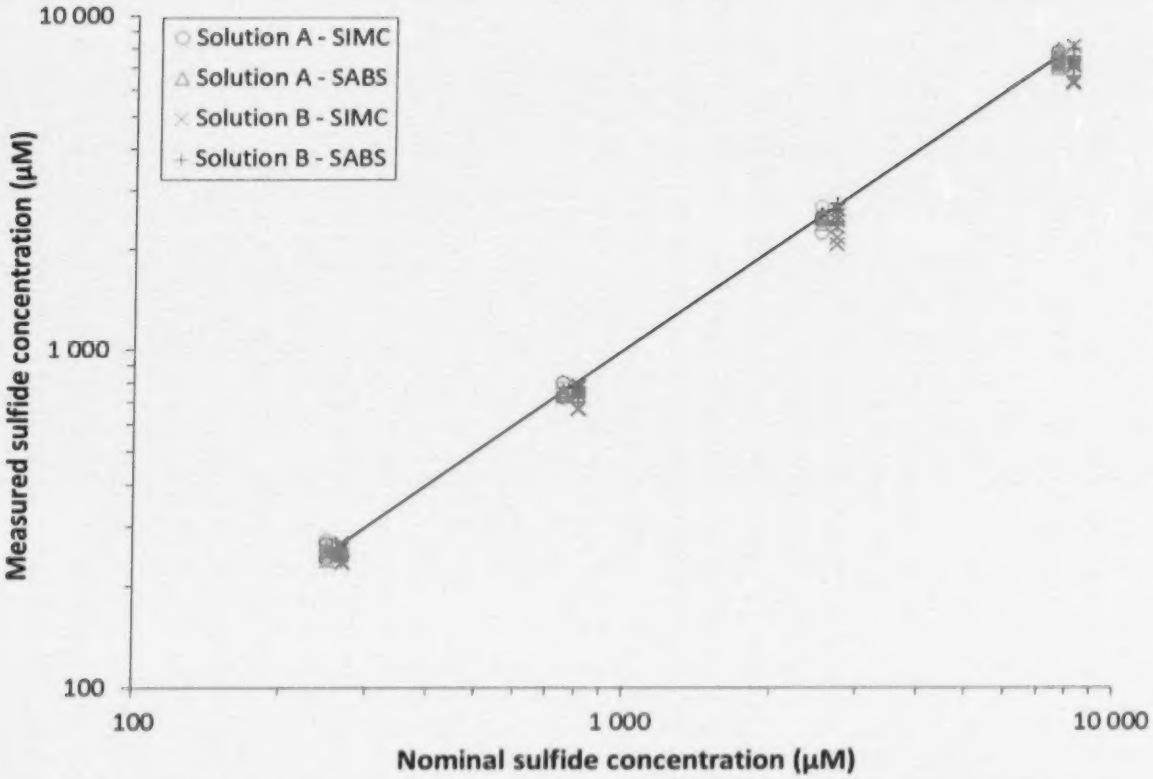

Fig. 2. Comparison of electrode filling solutions: nominal vs. measured sulfide concentrations (log_{10}-transformed) in test solutions measured with Thermo Orion silver/sulfide electrodes using Orion Optimum Results A and B filling solutions. Experiments were conducted at 2 labs (SIMC and SABS), 6 replicate trials per lab. The line represents a 1:1 ratio. Points for filling solution B (blue) have been offset to the right.

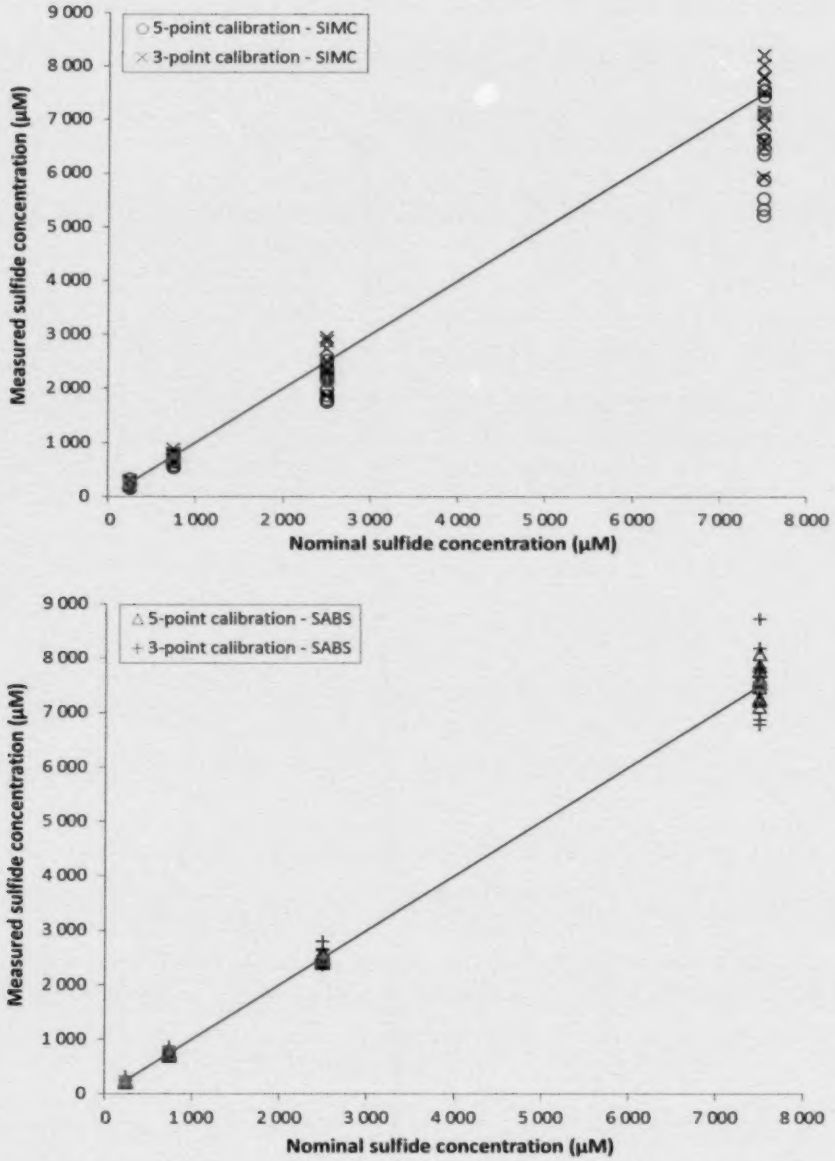
5-point calibration - SIMC
3-point calibration - SIMC
Measured sulfide concentration (µM)
Nominal sulfide concentration (µM)
5-point calibration - SABS
3-point calibration - SABS
Measured sulfide concentration (µM)
Nominal sulfide concentration (µM)

Fig. 3. Number of calibration standards: nominal vs. measured sulfide concentrations in test solutions measured with Thermo Orion silver/sulfide electrodes that were calibrated using 5 vs. 3 standard solutions. For the 5-point calibration, the sulfide standards were 100, 500, 1 000, 5 000, and 10 000 µM. For the 3-point calibration, the standards were 100, 1 000, and 10 000 µM. Experiments were conducted at 2 labs (SIMC and SABS), 12 replicate trials per lab. Top: SIMC results. Bottom: SABS results. The lines represent 1:1 ratios. Red symbols are mean values.

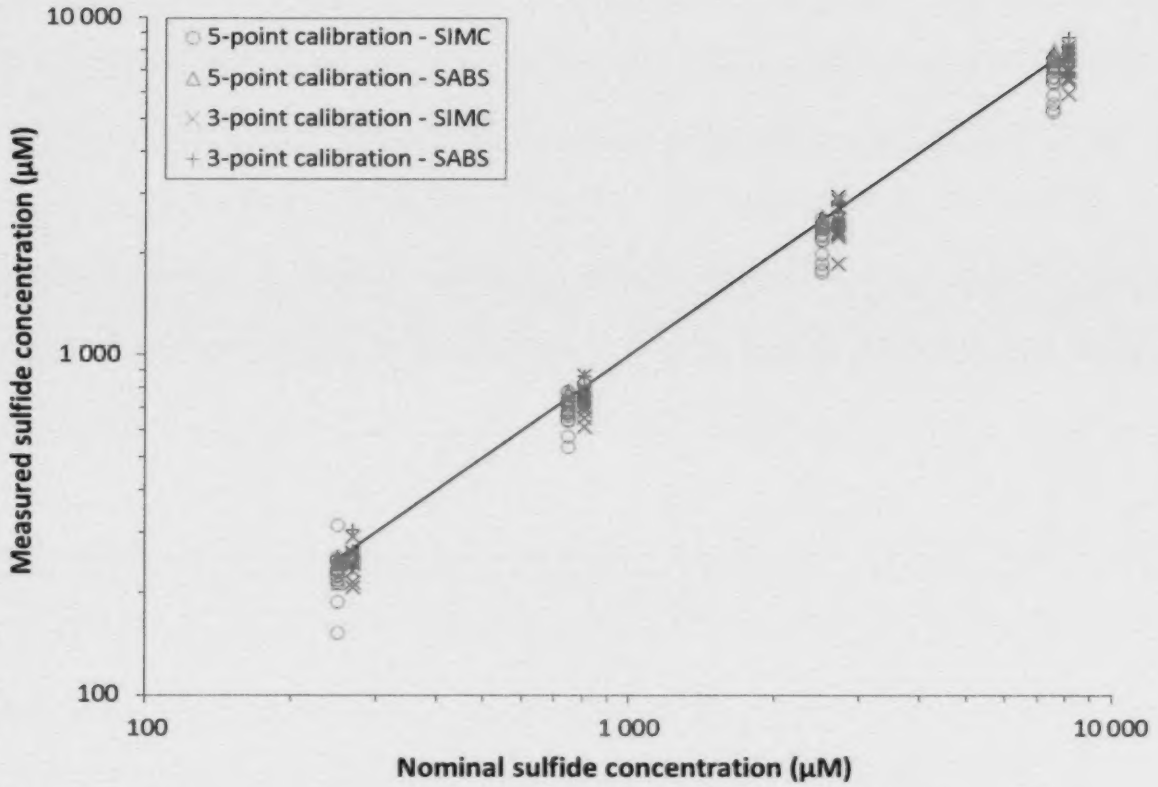

Fig. 4. Number of calibration standards: nominal vs. measured sulfide concentrations (log_{10}-transformed) in test solutions measured with Thermo Orion silver/sulfide electrodes calibrated using 5 vs. 3 standard solutions. For the 5-point calibration, the sulfide standards were 100, 500, 1 000, 5 000, and 10 000 µM. For the 3-point calibration, the standards were 100, 1 000, and 10 000 µM. Experiments were conducted at 2 labs (SIMC and SABS), 12 replicate trials per lab. The line represents a 1:1 ratio. Points for 3-point calibration (blue) have been offset to the right.

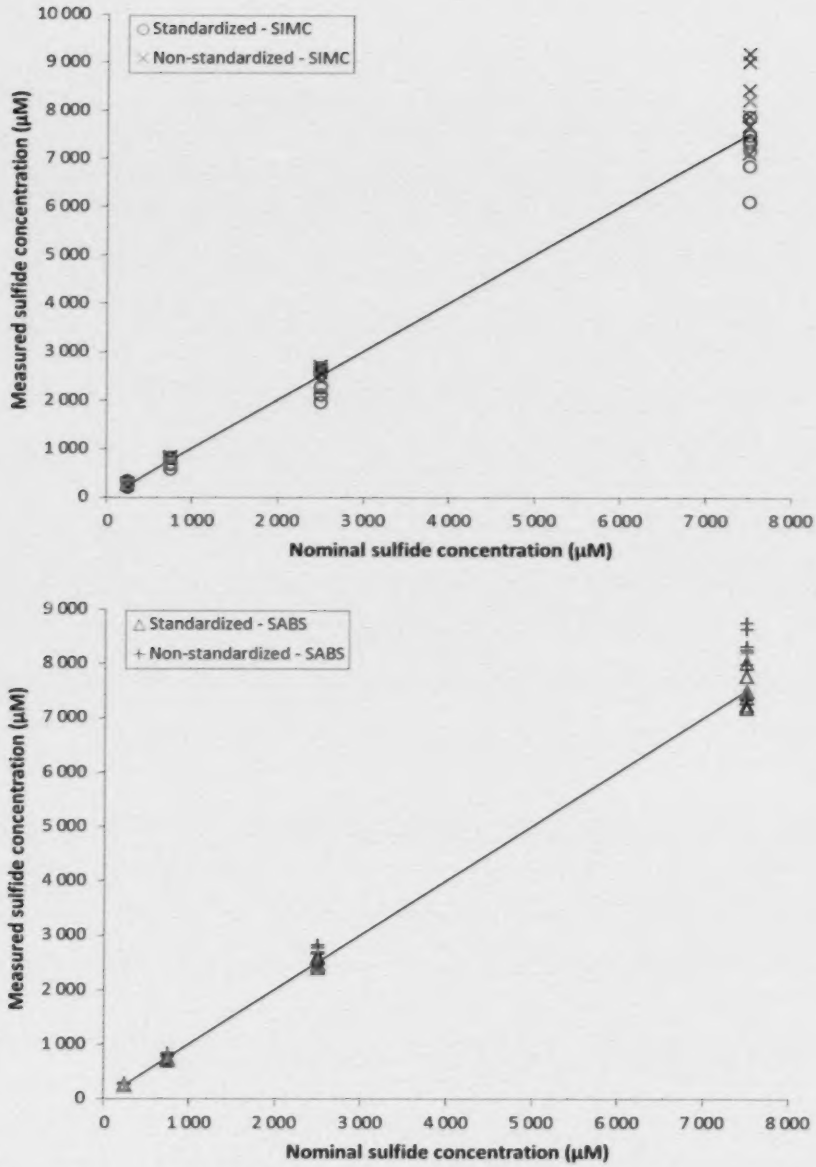

Fig. 5. Standardized vs. non-standardized calibration: nominal vs. measured sulfide concentrations in test solutions measured with Thermo Orion silver/sulfide electrodes using standardized vs. non-standardized calibration solutions. Experiments were conducted at 2 labs (SIMC and SABS), 6 replicate trials per lab. Top: SIMC results. Bottom: SABS results. The lines represent 1:1 ratios. Red symbols are mean values.

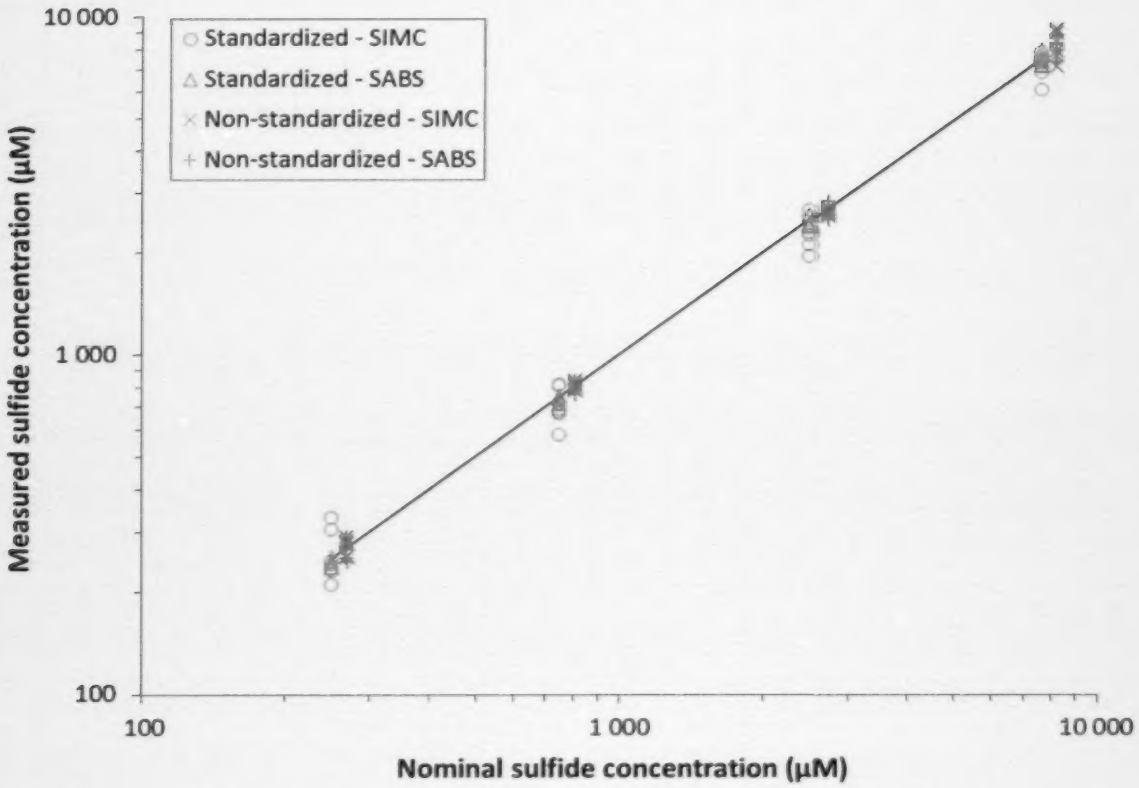

Fig. 6. Standardized vs. non-standardized calibration: nominal vs. measured sulfide concentrations (log_{10}-transformed) in test solutions measured with Thermo Orion silver/sulfide electrodes calibrated using standardized vs. non-standardized calibration solutions. Experiments were conducted at 2 labs (SIMC and SABS), 6 replicate trials per lab. The line represents a 1:1 ratio. Points for non-standardized calibration (blue) have been offset to the right.

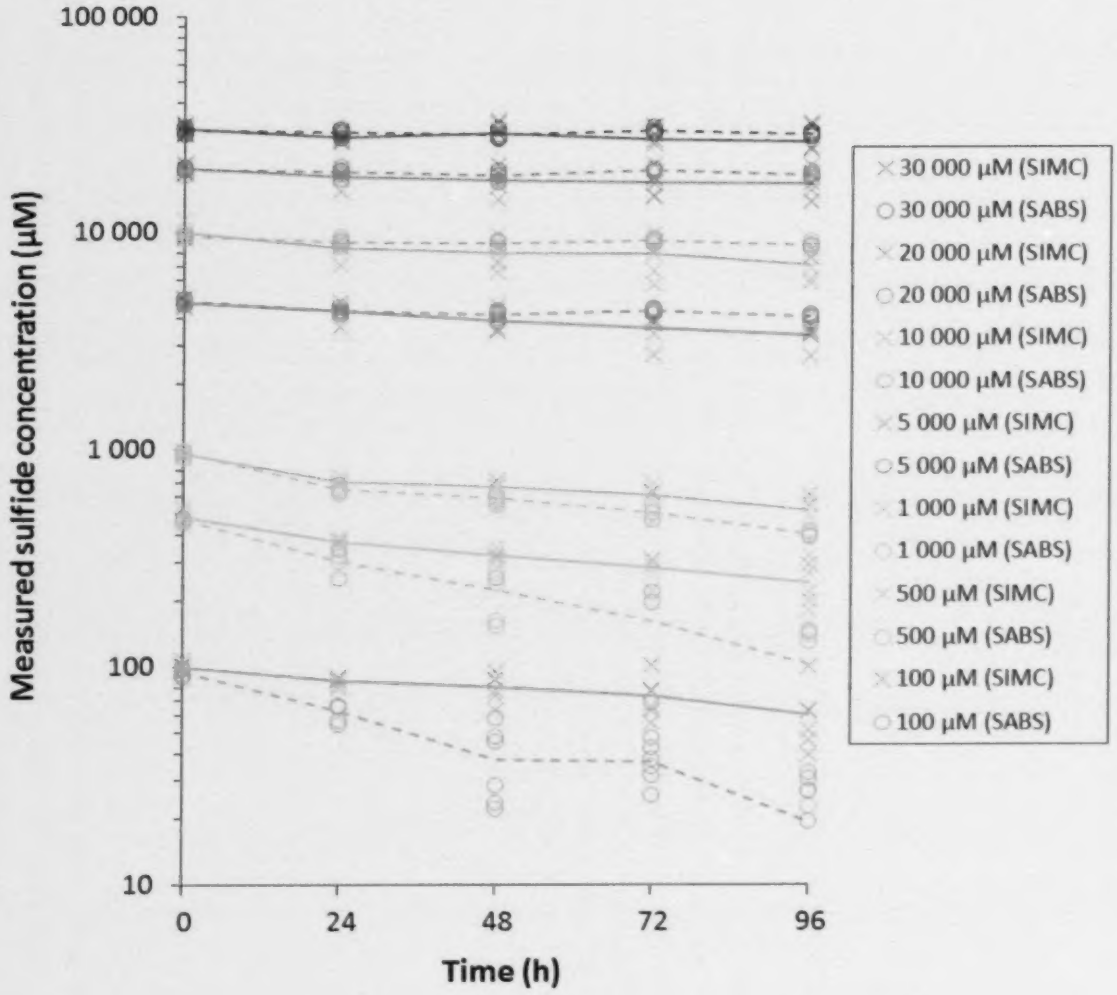

Fig. 7. Degradation of standard solutions. Test standards were prepared at sulfide concentrations of 100, 500, 1 000, 5 000, 10 000, 20 000, and 30 000 µM and measured at 0, 24, 48, 72, and 96 h. Electrodes were recalibrated for each measurement time. Experiments were conducted at two labs (SIMC and SABS), 6 replicate trials per lab, except only 5 replicates at SABS 72 h tests at 10 000-30 000 µM. Lines connect mean values for SIMC trials (solid lines) and SABS trials (dashed lines).

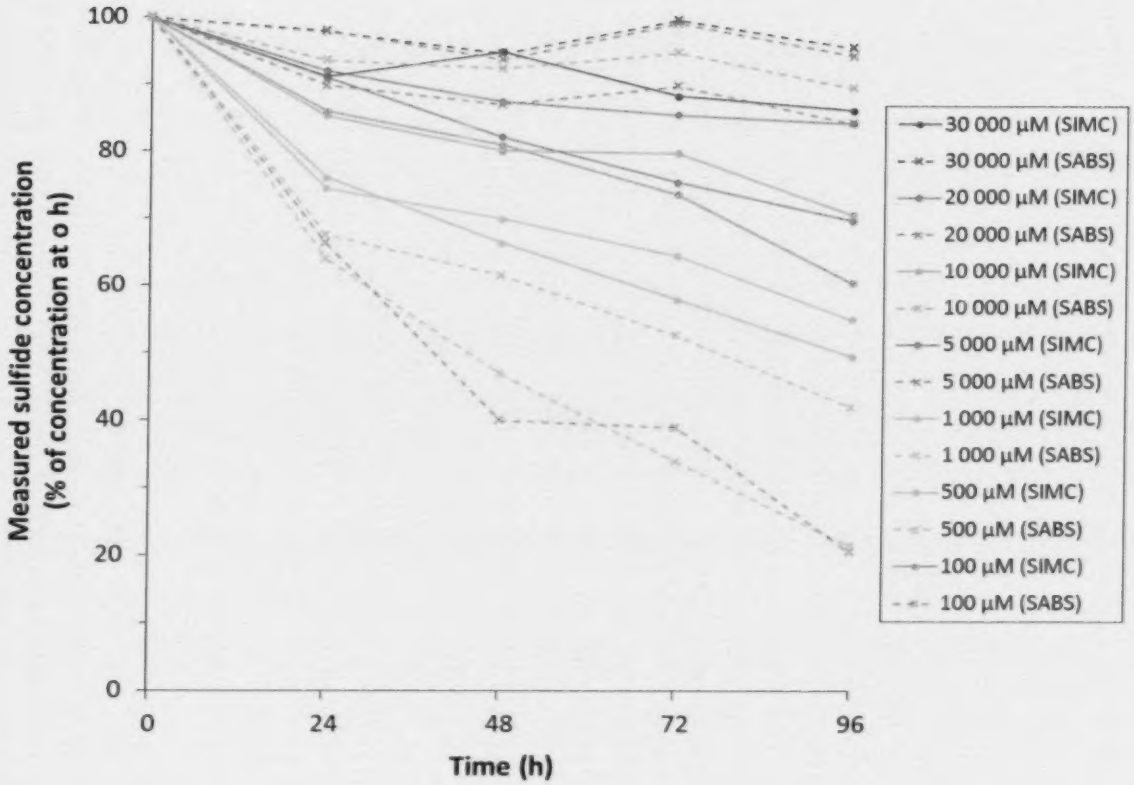

Fig. 8. Degradation of standard solutions, expressed as percent of measured sulfide concentration at 0 h. Test standards were prepared at sulfide concentrations of 100, 500, 1 000, 5 000, 10 000, 20 000, and 30 000 µM and measured after 0, 24, 48, 72, and 96 h. Electrodes were recalibrated for each measurement time. Experiments were conducted at two labs (SIMC and SABS), 6 replicate trials per lab, except only 5 replicates at SABS 72 h tests at 10 000-30 000 µM. Values shown are mean sulfide concentrations for each lab at each measurement time.

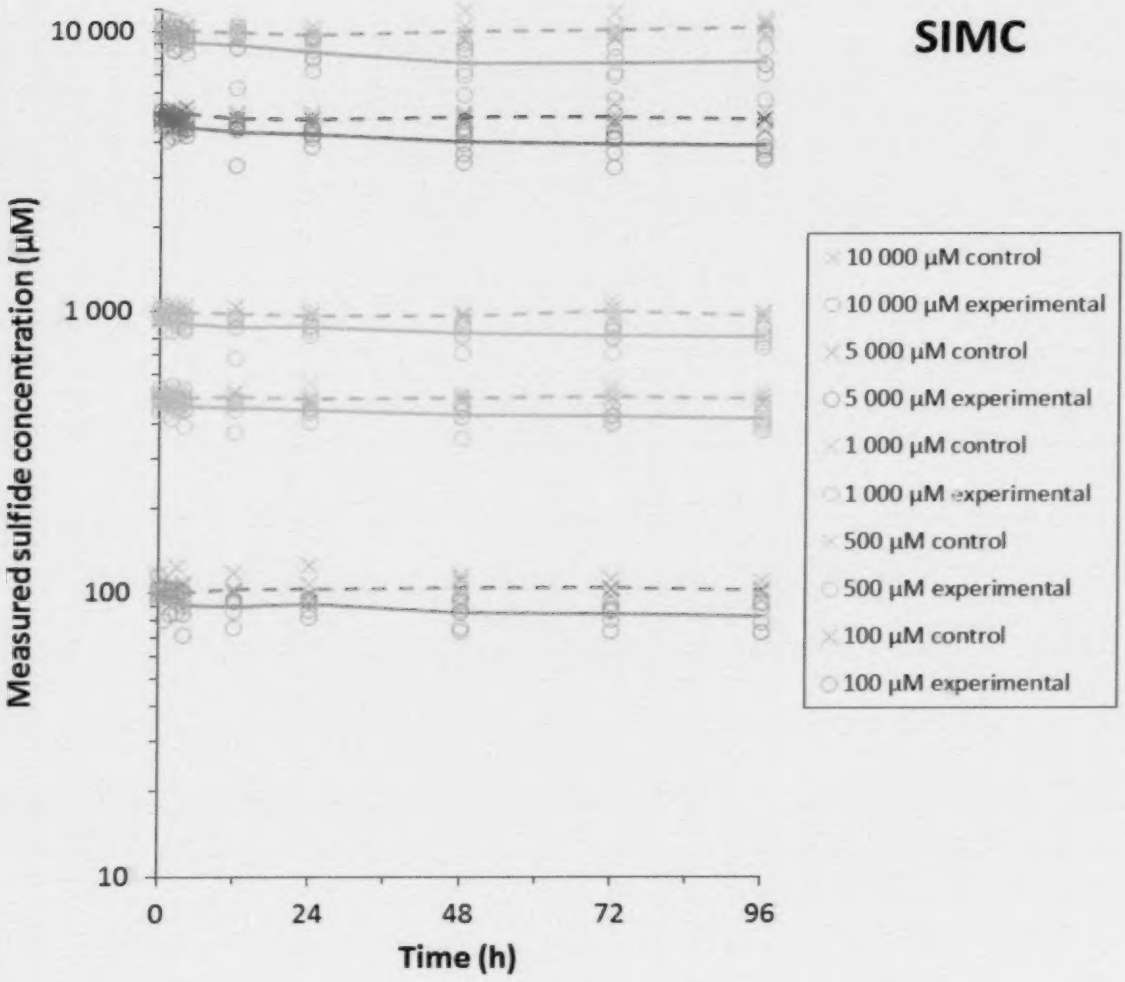

Fig. 9a. Electrode accuracy post-calibration in trials conducted at the SIMC lab. Sulfide concentrations were measured in test solutions (100, 500, 1 000, 5 000, and 10 000 µM) at 0, 1, 2, 3, 4, 12, 24, 48, 72, and 96 h post-calibration. Fresh stock solutions were used to prepare test solutions at 0, 24, 48, 72, and 96 h. Control electrodes (6 replicate trials) were recalibrated prior to each measurement time, except at 1 and 3 h. Experimental electrodes (6 replicate trials) were calibrated prior to the first measurement (0 h) only. Lines connect mean values for control electrodes (dashed lines) and experimental electrodes (solid lines).

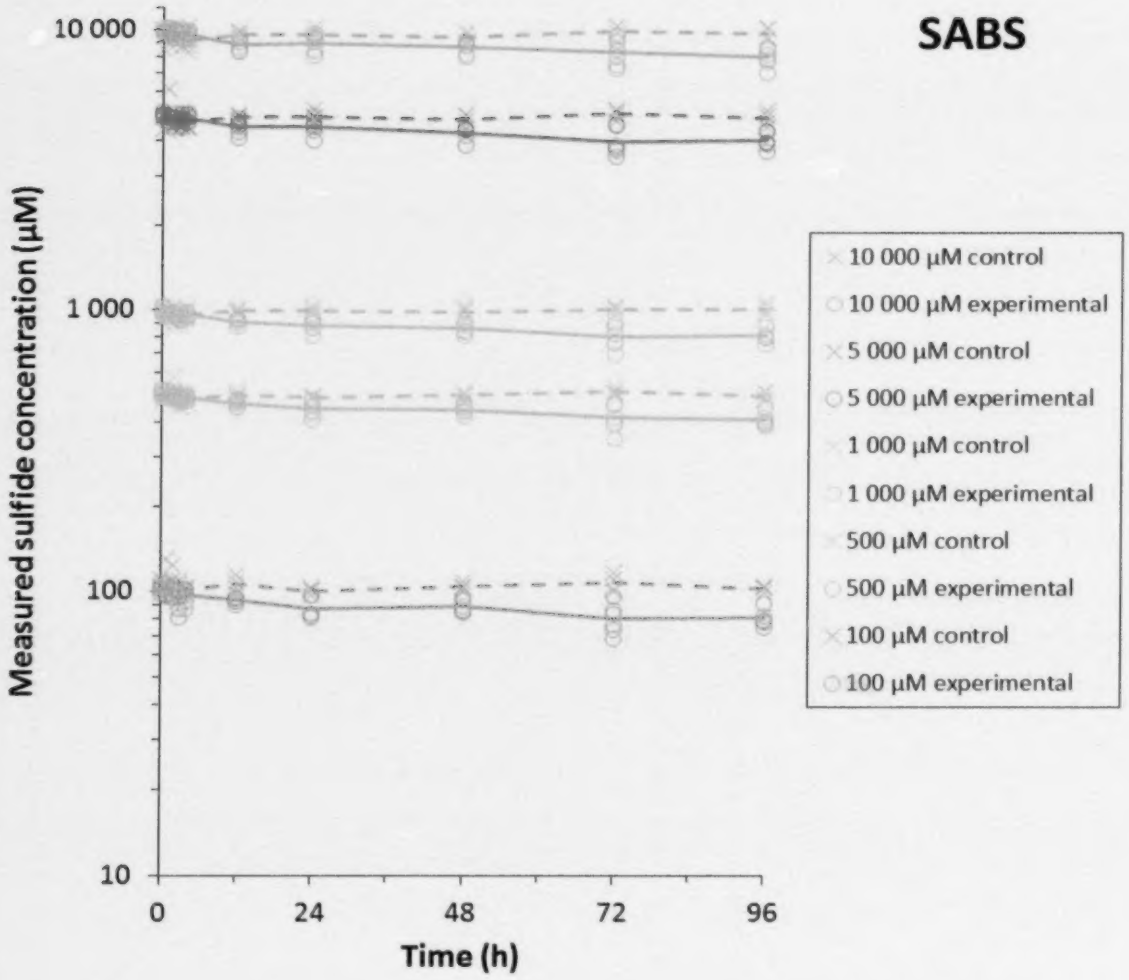

Fig. 9b. Electrode accuracy post-calibration in trials conducted at the SABS lab. Sulfide concentrations were measured in test solutions (100, 500, 1 000, 5 000, and 10 000 µM) at 0, 1, 2, 3, 4, 12, 24, 48, 72, and 96 h post-calibration. Fresh stock solutions were used to prepare test solutions at 0, 24, 48, 72, and 96 h. Control electrodes (4 replicate trials) were recalibrated prior to each measurement time, except at 1 and 3 h. Experimental electrodes (6 replicate trials) were calibrated prior to the first measurement (0 h) only. Lines connect mean values for control electrodes (dashed lines) and experimental electrodes (solid lines).

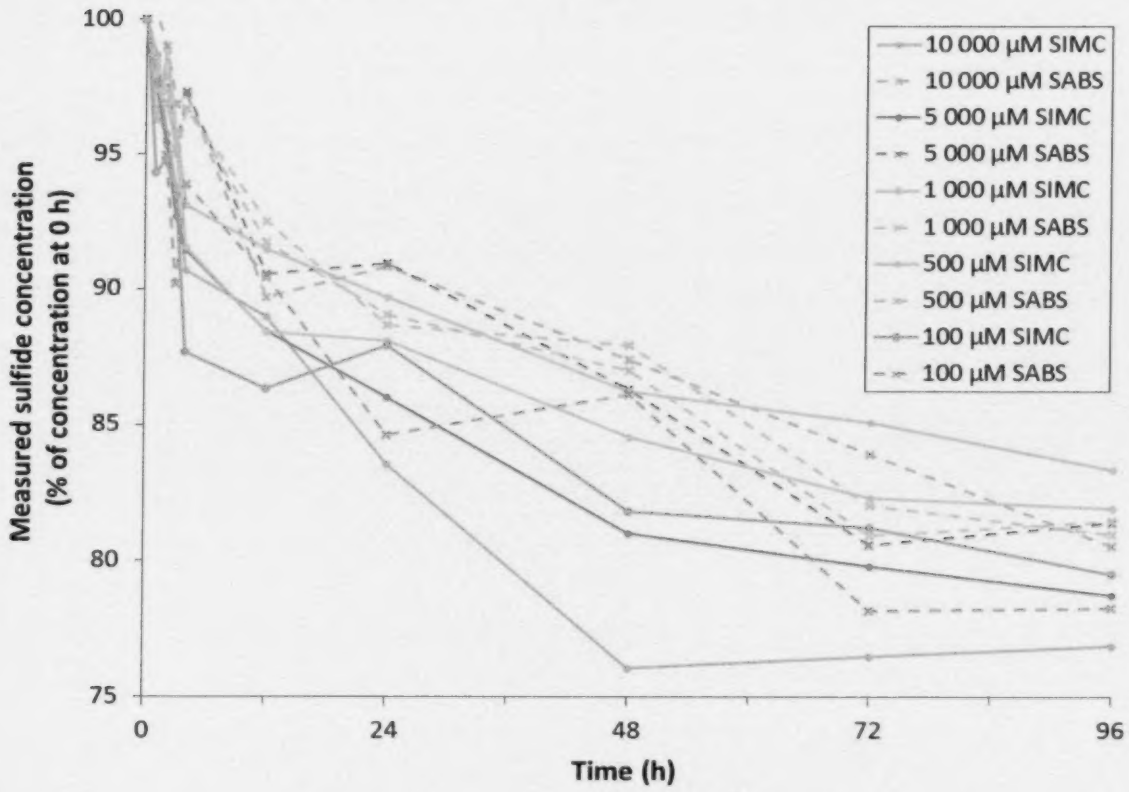

Fig. 10. Electrode accuracy post-calibration, expressed as percent of measured sulfide concentration at 0 h. Sulfide concentrations were measured in test solutions (100, 500, 1 000, 5 000, and 10 000 µM) at 0, 1, 2, 3, 4, 12, 24, 48, 72, and 96 h post-calibration. Fresh stock solutions were used to prepare test solutions at 0, 24, 48, 72, and 96 h. Experimental electrodes were calibrated prior to the first measurement (0 h) only. Experiments were conducted at two labs (SIMC and SABS), 6 replicate trials at each lab. Values shown are mean sulfide concentrations for experimental electrodes at each lab at each measurement time. Data for control electrodes are not shown (see Fig. 9a & 9b).

Appendix A. Detailed methods

1. Equipment used

- Meter: Accumet AP125 portable pH/ORP/ion meter (Fisher Scientific)
- Electrode: Orion Combination silver/sulfide ion electrode (Thermo Scientific, model 9616BNWP)
- Polishing strips for solid state ion selective electrodes (Thermo Scientific, cat. no. 948201)
- Temperature probe: Fisher Scientific Automatic Temperature Compensation probe AP60 series for Accumet meter (Fisher Scientific Cat. no. 13-620-AP53)

2. Chemicals used

- Sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$), crystalline form
  - SIMC: EMD Chemicals Inc, ACS grade, CAS 1313-84-4, cat. no. CASX0770-1
  - SABS: Sigma-Aldrich, ACS grade (≥ 98%), CAS 1313-84-4, cat. no. 208043
- Lead (II) perchlorate trihydrate [$Pb(ClO_4)_2 \cdot 3H_2O$], crystalline form
  - Both labs: Alfa Aesar, ACS grade (min. 97%), CAS 13453-62-8, cat. no. 11640
- Sodium hydroxide (NaOH), pellet form
  - SIMC: BDH, ACS grade (≥ 97%), CAS 1310-73-2, cat. no. CABDH0292
  - SABS: Sigma-Aldrich, ACS grade (≥ 97%), CAS 1310-73-2, cat. no. 221465
- Ethylenediaminetetraacetic (EDTA), powder form
  - SIMC: BDH, ACS grade (99.4 to 100.6%), CAS 60-00-4, cat. no. CABDH0232
  - SABS: Sigma-Aldrich, ACS grade (99.4 to 100.6%), CAS 60-00-4, cat. no. E9884
- L-ascorbic acid, powder form
  - SIMC: BDH, 99% min, CAS 50-81-7, cat. no. CABDH0242
  - SABS: Fisher Scientific, USP/FCC grade, CAS 50-81-7, cat. no. A62
- Orion Optimum Results B electrode filling solution (Thermo Scientific, cat. no. 900062)
- Orion Optimum Results A electrode filling solution (Thermo Scientific, cat. no. 900061)

Appendix A. Detailed methods

3. Preparation of reagents and chemicals

3.1 Degassed water

SIMC: Millipore water (18.2 MΩ·cm) was boiled for 15 min and transferred to Nalgene bottles for storage.

SABS: Milli-Q water (18.2 MΩ·cm, *c.* 4 L) was boiled on a hotplate for *c.* 30 min then transferred to Pyrex media bottles (2 L & 1 L bottles). Bottles were completely filled to eliminate headspace, capped tightly, then allowed to cool ambient temperature prior to use. Alternatively, Milli-Q water was sparged overnight with helium gas whilst being magnetically stirred on a stir plate.

3.2 Sulfide anti-oxidation buffer (SAOB)

Sodium hydroxide (*c.* 160 g) was weighed into a 2 L volumetric flask, some degassed water was added, and the flask was swirled to aid dissolution. Once dissolved, the solution was allowed to cool down prior to addition of EDTA. EDTA (*c.* 150 g) was weighed into a beaker then transferred to the sodium hydroxide solution. The beaker was rinsed several times with degassed water and the washings were transferred to the flask. More degassed water was added to the flask and the solution was swirled to aid dissolution of the EDTA (at SABS, the solution was sonicated, if required). The solution was then made up to volume, capped and gently inverted several times to obtain a homogenous solution. It was then transferred to a media bottle, capped, and stored at *c.* +4°C until used.

3.3 Ascorbic acid

Aliquots (0.875 g) of ascorbic acid were weighed into 60 mL amber vials (SIMC) or 50 mL test tubes (SABS).

4. Preparation of sulfide electrode for use

Approximately 24 h prior to use, the sulfide electrode was rinsed with filling solution, then filled with filling solution to below the fill hole. The electrode was then stored in a solution containing degassed water and a few drops of the filling solution. Filling solution B was used, except in the experiment comparing filling solutions, where each trial included one electrode filled with solution A and one electrode filled with solution B. At SIMC, small amounts of filling solution were expelled from the tip of the electrode to eliminate bubbles surrounding the membrane; at SABS, no bubbles were formed.

The sensing surface of the electrode was cleaned prior to use. This was achieved by holding the electrode inverted, adding a drop or two of degassed water to the sensing surface. A piece of polishing strip (shiny side up) was placed on the sensing surface, held with light pressure then the electrode rotated for *c.* 30 seconds to polish the surface. The electrode was then rinsed and placed back into the storage solution.

Appendix A. Detailed methods

5. Preparation of sodium sulfide stock solution (0.0429 M)

Fresh Na_2S stock solutions (100 mL) were prepared daily prior to use unless otherwise stated. Sodium sulfide (*c.* 1.030 g) was weighed (at SIMC, into an antistatic polystyrene weighing canoe; at SABS, into a glass weigh boat) and then quantitatively transferred to a 100 mL amber volumetric flask using degassed water. The flask was swirled gently to aid dissolution of the Na_2S then made up to the mark with further degassed water, capped, then gently inverted a few times to obtain a homogenous solution. The stock solution was stored in amber bottles until used (in the refrigerator at SIMC; not at SABS as stock was used quickly after preparation).

The Na_2S used by SIMC was a larger granular size and required pulverizing with a mortar and pestle (prior to dissolution). The resulting smaller crystals were stored in an amber bottle in a desiccator for up to 3 weeks.

6. Preparation of lead (II) perchlorate (0.1 M)

Fresh lead (II) perchlorate solutions were prepared daily prior to use unless otherwise stated. Lead (II) perchlorate (*c.* 2.301 g) was weighed (at SIMC, into an antistatic polystyrene weighing canoe; at SABS, into a glass weigh boat) and then quantitatively transferred to a 50 mL amber volumetric flask using degassed water. The flask was swirled gently to aid dissolution of the lead (II) perchlorate, then made up to the mark with further degassed water, capped, then gently inverted a few times to obtain a homogenous solution. The solution was stored in amber bottles until used.

7. Titration of sodium sulfide stock solution

The sulfide concentration of the prepared $Na_2S{\cdot}9H_2O$ stock solution was determined by titrating it against the prepared lead (II) perchlorate solution as follows.

A solution of SAOB/ascorbic acid was prepared by dissolving 0.875 g of ascorbic acid with 25 mL SAOB and mixing well until all appeared to be dissolved (at SIMC the solution was swirled until dissolved; at SABS the solution was vortexed to aid dissolution, then sonicated briefly to remove any air bubbles in solution). Twenty-five millilitres (25 mL) of the prepared $Na_2S{\cdot}9H_2O$ standard was combined with the SAOB/ascorbic solution in a 100 mL beaker containing a magnetic stir bar. The prepared electrode was immersed in the solution then clamped in place. The meter was set to 'mV' and gentle stirring started. Once the reading had stabilized, the mV reading was recorded and the titration performed (at SIMC, using a burette; at SABS, by pipette) adding the following volumes of the prepared lead (II) perchlorate solution into the beaker: 2 mL, 2 mL, 2 mL, 2 mL, 1 mL, 1 mL then 0.1 mL added continuously until the end point was reached. The inflection point is the point at which the greatest change in mV reading was obtained for the volume of titrant added.

If titrating older batches of $Na_2S{\cdot}9H_2O$, the volumes of lead (II) perchlorate for titration may need to be adjusted accordingly to e.g. 2, 2, 2, 2, 1, 0.5, 0.1, 0.1 mL, etc. When the end point is nearly reached, the mV reading will increase then drop again. It could take at least 10 min for the reading to stabilize before the next volume of lead (II) perchlorate can be added.

The sulfide concentration was calculated using the following equation:

Appendix A. Detailed methods

$$V_{Pb(ClO_4)_2} \cdot C_{Pb(ClO_4)_2} = V_{Na_2S} \cdot C_{Na_2S}$$

(where V = volume and C = concentration). After the titration was complete, the sensing surface of the electrode was cleaned with a piece of polishing strip to remove any contamination.

8. Calibration procedure

On the day of use, the sensing membranes were cleaned with a piece of polishing strip prior to use. Based on the calculated sulfide concentration in the stock solution (see section 7), a set of standards was prepared with the following dilution scheme, using degassed water as the diluent:

Standard	Standard used	Volume used (mL)	Final volume (mL)	Sulfide concentration (μM)
A	Stock	X	10	10 000
B	A	5	10	5 000
C	B	2	10	1 000
D	C	5	10	500
E	D	2	10	100

X = volume required determined from titration

Five millilitres (5 mL) of each standard was transferred into separate 60 mL amber bottles (SIMC) or 20 mL scintillation vials (SABS). SAOB/ascorbic acid solution was prepared by adding SAOB (25 mL) to ascorbic acid (0.875 g) in a test tube or graduated cylinder. The solution was mixed (at SIMC, swirled until dissolved; at SABS, vortex mixed and briefly sonicated), aliquots (5 mL) added to each vial containing standard, then gently swirled to mix.

The temperature probe was connected to the meter along with the electrode. Calibration was performed between 20°C to 25°C according to the meter manufacturer's instructions. The electrode and temperature probe were immersed into the 100 μM standard, gently swirled, and the mV reading was allowed to stabilize. Once a stable reading was obtained, the value was accepted and the temperature recorded – all calibrations and test readings were performed at this temperature. The electrode and temperature probe were rinsed with degassed water then immersed into the next highest concentration standard and the calibration steps repeated. This was repeated until the meter had been calibrated with all five standards. Warming the sample by hand or cooling with an ice bath as required helped with obtaining the temperature required for calibration and test sample analysis.

Since the Accumet meter employs segmented calibration rather than least squares linear regression, the point-to-point slopes (i.e. standard E to D, D to C, C to B, B to A) should be recorded as well. These slopes are displayed after the mV readings are accepted into the meter during the calibration procedures and should be between -27 and -33. Slope differences between the 500 and 5 000 μM standards and between the 1 000 and 10 000 μM standards should be between 25 to 30 mV. If either of these checks is outside the acceptable ranges, then the electrode must be recalibrated.

Appendix A. Detailed methods

9. Experiments

9.1 General experimental test procedures

At SIMC, various combinations of meters and electrodes were used. In all, 9 meters and 10 electrodes were used. Three of the electrodes were new (used in sediment <3 times prior to this study) and the others were older.

At SABS, three instrument set-ups were used:

- Combination 1 = meter 1 + electrode 1 + temperature probe 1
- Combination 2 = meter 2 + electrode 2 + temperature probe 2
- Combination 3 = meter 3 + electrode 3 + temperature probe 3

For all SABS experiments except the electrode accuracy post-calibration study, measurements were conducted by two analysts, one using equipment combination 1 and the other using combination 2. Equipment combination 3 was used only as the control in the experiment on electrode accuracy post-calibration. All 3 of the electrodes at SABS were new.

At both labs, 6 replicate trials were conducted for each experiment, except in the experiment examining the number of calibration standards, where 12 replicate trials were conducted. Except where noted, measurements were recorded for both sulfide concentration (μM) and electrode potential (mV).

Experimental test solutions were prepared from the $Na_2S{\cdot}9H_2O$ stock solution by dilution with degassed water. See below for dilution schemes specific to each experiment. Five millilitres (5 mL) of each test solution was transferred into separate 60 mL amber bottles (SIMC) or 20 mL scintillation vials (SABS).

A fresh solution of SAOB/ascorbic acid was prepared by pipetting SAOB (25 mL) into a test tube containing ascorbic acid (0.875 g). This was capped and mixed (at SIMC, swirled until dissolved; at SABS, vortex mixed, then sonicated briefly) before aliquots (5 mL) were added to each test solution before analysis.

The sulfide electrode and temperature probe were immersed into the weakest test solution and a stable ion and mV reading taken at the temperature that the calibration was performed. The sulfide electrode and temperature probe were then rinsed with degassed water and the analysis procedure repeated with the remaining test solutions. Warming the test solution by hand or cooling with an ice bath as required helped with obtaining the temperature required for calibration and test analysis.

9.2 Comparison of electrode filling solutions

Each replicate trial consisted of two electrodes, one for each treatment: one electrode was prepared with Optimum Results A filling solution and a second electrode with Optimum Results B.

Appendix A. Detailed methods

Electrodes were prepared and calibrated following methods described above in sections 4 to 8. General experimental test procedures are described in section 9.1. Test solutions were prepared from the Na_2S stock solution using the following dilution scheme:

Test solution	Solution Used	Volume used (mL)	Final volume (mL)	Sulfide concentration (μM)
1	Stock	X	10	7 500
2	1	3.33	10	2 500
3	2	3	10	750
4	3	3.33	10	250

X = volume required determined from titration

One set of test solutions (5 mL aliquots) was used to test two electrodes, one for each treatment.

Six replicate trials were conducted at each lab; in each replicate trial, one electrode used filling solution A and the other electrode used filling solution B. At SIMC, various meter/probe combinations were used. At SABS, equipment combinations 1 & 2 were used concurrently; each equipment combination was used for 3 replicates using filling solution A and 3 replicates using filling solution B.

9.3 Number of calibration standards (5 vs. 3-point calibration)

Each replicate trial consisted of two electrodes, one for each treatment: one electrode was calibrated using 5 standards and a second electrode was calibrated using 3 standards.

Electrodes were prepared and calibrated following methods described above in sections 4 to 8, except the second electrode was calibrated using only 3 sulfide standards (100, 1 000, and 10 000 μM). General experimental test procedures are described above in section 9.1. The test solution dilution scheme was the same as in section 9.2. One set of test solutions (5 mL aliquots) was used to test two electrodes, one for each treatment.

Twelve replicate trials were conducted at each lab; in each replicate trial, one electrode was calibrated with 5 standards and one electrode was calibrated with 3 standards. At SIMC, various meter/probe combinations were used. At SABS, equipment combinations 1 & 2 were used concurrently; each equipment combination was used in 6 replicates using 5-point calibration and 6 replicates using 3-point calibration.

9.4 Standardized vs. non-standardized calibration (titration vs. mathematical calculation of stock solution concentration)

Each replicate trial consisted of two electrodes, one for each treatment: one electrode was calibrated using standards prepared from standardized Na_2S stock solution (concentration determined by titration) and a second electrode was calibrated using standards prepared from non-standardized stock solution (concentration mathematically calculated).

Appendix A. Detailed methods

The electrode that was calibrated using standardized stock solution (using titration) was prepared and calibrated following methods described above in sections 4 to 8. The electrode that was calibrated using non-standardized stock solution was prepared and calibrated following the same methods, except titration was omitted. The sulfide concentration (in Molarity) for the non-standardized stock solution was determined based on the weight of Na_2S and the volume of diluent water:

$$[S^{2-}] = \frac{Na_2S \cdot 9H_2O \text{ weight (g)}}{240.18} \times \frac{1000}{\text{flask vol. (mL)}}$$

Each set of calibration standards (one prepared from standardized stock solution and one prepared from non-standardized stock solution) was used to calibrate one electrode.

General experimental test procedures are described above in section 9.1. The test solution dilution scheme was the same as in section 9.2. One set of test solutions (5 mL aliquots) was used to test two electrodes, one for each treatment.

Six replicate trials were conducted at each lab; each trial included one electrode that was calibrated using standardized standards and one electrode that was calibrated using non-standardized standards. At SIMC, various meter/electrode combinations were used. At SABS, equipment combinations 1 & 2 were used concurrently; each equipment combination was used in 3 replicates using standardized calibration and 3 replicates using non-standardized calibration.

9.5 Degradation of standard solutions

In each replicate trial, one electrode was used to measure the sulfide concentration in 7 test standard solutions (100-30 000 µM) after storage times of 0, 24, 48, 72, and 96 h.

Electrodes were prepared and calibrated at each test storage time, following methods described above in sections 4 to 8 (except a larger volume of stock solution was prepared). General experimental test procedures are described in section 9.1.

At SABS, test standard solutions were prepared from the Na_2S stock solution using the following dilution scheme:

Test standard solution	Solution Used	Volume used (mL)	Final volume (mL)	Sulfide concentration (µM)
1	Stock	X	50	30 000
2	Stock	X	50	20 000
3	1	16.67	50	10 000
4	2	12.5	50	5 000
5	3	5	50	1 000
6	4	5	50	500
7	5	5	50	100

X = volume required determined from titration

Appendix A. Detailed methods

The initial (0 h) sulfide concentration in each test standard solution was measured (see section 9.1). The remaining test standard solutions were then taken up into replicate 5 mL syringes and any air bubbles and excess solution purged until 5 mL aliquots remained. The tips were then sealed with Parafilm® to prevent any oxidation and stored at *c.* +4°C in the dark. At the test storage times (24, 48, 72, and 96 h), one syringe from each concentration was removed from storage then dispensed into separate 20 mL vials prior to analysis using freshly calibrated meters and electrodes.

At SIMC, test standard solutions were prepared in 500 mL volumetric flasks, by serial dilution from the stock solution. From these flasks, 5 sets of test standard solutions were dispensed into 20 mL amber bottles (with no head space) and kept in the refrigerator. At each test time (0, 24, 48, 72, and 96 h), one set of test standard solutions was removed from the refrigerator. Five millilitre (5 mL) aliquots of each were dispensed into 60 mL amber bottles, then 5 mL of SAOB/ascorbic acid solution was added to each bottle and mixed gently. A freshly calibrated electrode was used to take measurements in each of the 7 test standard solutions, starting with the weakest, at each test storage time.

Six replicate trials were conducted at each lab. At SIMC, various meter/electrode combinations were used. At SABS, equipment combinations 1 & 2 were used concurrently; each equipment combination was used in 3 replicate trials.

9.6 Electrode accuracy post-calibration

In each replicate trial, one electrode (the experimental electrode) was used to measure sulfide concentration in 5 test solutions at 0, 1, 2, 3, 4, 12, 24, 48, 72, and 96 h post-calibration. Simultaneous measurements were also taken with a control electrode which was recalibrated throughout the test period.

Electrodes were prepared and calibrated at time 0 h, following methods described above in sections 4 to 8 (except a larger volume of stock solution was prepared). At SABS, the fill holes of the electrodes were covered with Parafilm® to reduce fill solution evaporation over the 96 h.

General experimental test procedures are described in section 9.1. Test solutions were prepared from the Na_2S stock solution using the following dilution scheme:

Test solution	Solution Used	Volume used (mL)	Final volume (mL)	Sulfide concentration (µM)
1	Stock	X	10	10 000
2	1	5	10	5 000
3	2	2	10	1 000
4	3	5	10	500
5	4	2	10	100

X = volume required determined from titration

One set of test solutions (5 mL aliquots) was used for measurements by control and experimental electrodes at each measurement time.

Appendix A. Detailed methods

One stock solution was used to prepare test solutions at 0, 1, 2, 3, 4, and 12 h. This stock solution was titrated (to check sulfide concentrations) at 0, 2, 4, and 12 h, using lead (II) perchlorate prepared at 0 h. Test solutions for times 24, 48, 72, and 96 h were prepared with fresh stock solutions and were titrated with freshly prepared lead (II) perchlorate solution. The control electrode was recalibrated at each measurement time, except at 1 and 3 h at SABS. The experimental electrode was calibrated only at 0 h. Each electrode was used to take measurements in each of the 5 test solutions, starting with the weakest, at each measurement time.

Six replicate trials were conducted at each lab. At SIMC, various meter/electrode combinations were used. At SABS, equipment combinations 1 & 2 were used as the experimental electrodes (three replicate trials with each). Combination 3 was used for controls in all trials, except there was no control electrode in the first trial with each of the experimental electrodes.

Appendix B. Comparison of electrode filling solutions: data tables

Equipment

Table B1. Meters and electrodes used in tests comparing electrode filling solutions.

Lab	Equipment ID	Meter	Sulfide Electrode	Lab	Equipment ID	Meter	Sulfide electrode
SIMC	A	837623	QZ1-11024	SABS	1	2007890	Q01-13710
	B	537447	OV1-16043		2	2042138	Q01-13706
	C	537447	OV1-16043				
	D	837623	QZ1-11024				
	E	2059868	QQ1-15961				
	F	486278	QZ1-11182				
	G	486278	RS1-15718				
	H	20077891	OW2-10925				
	I	837623	QZ1-11024				
	J	2059868	QQ1-15961				
	K	20077891	OW2-10925				
	L	486278	QZ1-11182				

SIMC electrode RS1-15718 was new and had been used less than 3 times in sediment.

Both SABS electrodes were new.

Appendix B. Comparison of electrode filling solutions: data tables

Calibration data

Table B2. Calibration data for tests comparing electrode filling solutions at SIMC. Values are measured electrode potentials (mV) in 5 calibration standards at SIMC.

Filling Solution	Replicate	Equip. ID	Calibration standard nominal sulfide concentration (µM)					Temp. (°C)
			100	500	1 000	5 000	10 000	
A	1	A	-766.4	-789.6	-798.3	-818.6	-826.9	21.3
A	2	C	-766.7	-789.0	-797.8	-817.8	-825.9	22.1
A	3	E	-768.6	-791.3	-800.0	-820.5	-828.8	22.6
A	4	G	-771.6	-792.6	-801.3	-821.0	-829.2	22.8
A	5	I	-768.6	-790.0	-798.9	-819.4	-827.5	22.4
A	6	K	-771.4	-792.1	-799.9	-819.7	-827.9	22.7
B	1	B	-851.5	-873.6	-882.2	-902.1	-910.3	21.4
B	2	D	-852.1	-874.3	-883.4	-903.2	-911.5	22.0
B	3	F	-854.3	-876.8	-885.3	-906.0	-913.3	21.8
B	4	H	-855.6	-875.4	-883.9	-903.8	-912.4	22.8
B	5	J	-855.0	-876.8	-885.6	-906.4	-914.6	22.9
B	6	L	-852.3	-873.6	-881.5	-900.9	-908.7	22.7

Table B3. Calibration data for tests comparing electrode filling solutions at SABS. Values are measured electrode potentials (mV) in 5 calibration standards at SABS.

Filling Solution	Replicate	Equip. ID	Calibration standard nominal sulfide concentration (µM)					Temp. (°C)
			100	500	1 000	5 000	10 000	
A	1	1	-769.3	-791.1	-800.0	-820.3	-829.3	20.8
A	2	1	-769.3	-790.7	-799.6	-819.7	-828.9	20.8
A	3	1	-768.7	-790.2	-798.8	-818.7	-826.4	20.8
A	4	2	-763.9	-787.2	-796.3	-816.3	-825.1	21.0
A	5	2	-765.8	-787.7	-796.5	-816.3	-825.3	20.9
A	6	2	-766.1	-788.0	-796.9	-816.9	-825.6	20.9
B	1	2	-849.2	-873.4	-882.2	-903.4	-912.1	20.8
B	2	2	-850.4	-872.6	-882.0	-902.0	-910.3	20.8
B	3	2	-852.4	-873.0	-881.3	-901.0	-909.6	21.0
B	4	1	-852.3	-874.7	-883.4	-904.3	-912.9	21.0
B	5	1	-852.9	-874.6	-883.6	-903.8	-912.3	20.7
B	6	1	-852.0	-874.7	-883.1	-903.3	-912.3	20.8

Appendix B. Comparison of electrode filling solutions: data tables

Test data

Table B4. Results from tests comparing electrode filling solutions at SIMC. Values are sulfide concentrations (µM) and electrode potentials (mV) measured in 4 test solutions.

Filling solution	Replicate	Equip. ID	Test solution nominal sulfide concentration (µM)							
			250		750		2 500		7 500	
			µM	mV	µM	mV	µM	mV	µM	mV
A	1	A	268	-781.0	771	-795.3	2 450	-809.9	7 140	-823.1
A	2	C	265	-779.7	733	-793.8	2 440	-808.8	7 480	-822.4
A	3	E	274	-782.8	794	-797.1	2 660	-812.4	7 680	-825.5
A	4	G	241	-783.2	721	-797.2	2 460	-812.3	7 780	-826.1
A	5	I	254	-781.0	718	-794.7	2 220	-809.1	7 410	-824.0
A	6	K	264	-783.8	801	-797.4	2 510	-811.1	7 250	-824.2
B	1	B	234	-863.0	668	-876.9	2 150	-891.3	6 320	-904.5
B	2	D	258	-856.1	784	-880.2	2 600	-895.1	8 070	-908.9
B	3	F	258	-868.1	736	-882.1	2 310	-896.9	7 000	-910.3
B	4	H	263	-867.6	779	-880.9	2 510	-895.2	7 190	-908.3
B	5	J	235	-866.9	664	-880.5	2 050	-894.9	6 230	-909.1
B	6	L	268	-865.3	769	-878.5	2 430	-892.2	7 070	-904.7

Table B5. Results from tests comparing electrode filling solutions at SABS. Values are sulfide concentrations (µM) measured in 4 test solutions. "–" indicates electrode potentials (mV) not recorded.

Filling solution	Replicate	Equip. ID	Test solution nominal sulfide concentration (µM)							
			250		750		2 500		7 500	
			µM	mV	µM	mV	µM	mV	µM	mV
A	1	1	248	–	744	–	2 490	–	7 410	–
A	2	1	255	–	752	–	2 540	–	7 100	–
A	3	1	252	–	757	–	2 450	–	7 910	–
A	4	2	256	–	730	–	2 380	–	7 230	–
A	5	2	240	–	737	–	2 510	–	6 970	–
A	6	2	262	–	755	–	2 460	–	7 690	–
B	1	2	247	–	697	–	2 400	–	6 500	–
B	2	2	239	–	723	–	2 350	–	7 470	–
B	3	2	236	–	772	–	2 710	–	7 920	–
B	4	1	242	–	733	–	2 370	–	7 120	–
B	5	1	238	–	721	–	2 400	–	7 270	–
B	6	1	239	–	749	–	2 600	–	7 880	–

Appendix C. Number of calibration standards (5 vs. 3-point): data tables

Equipment

Table C1. Meters and electrodes used in tests comparing 5 vs. 3-point calibration.

Lab	Equipment ID	Meter	Sulfide Electrode	Lab	Equipment ID	Meter	Sulfide Electrode
SIMC	A	2007891	OW2-10925	SABS	1	2007890	Q01-13710
	B	2059868	QQ1-15961		2	2042138	Q01-13706
	C	2059868	OW2-10925				
	D	2007891	QQ1-15961				
	E	537447	OV1-13043				
	F	837623	QZ1-11024				
	G	491819	QO1-13714				
	H	537447	OV1-13043				
	I	537447	QQ1-15961				
	J	491819	QO1-13714				
	K	837623	QZ1-11024				
	L	2059868	OW2-10925				
	M	2059868	QQ1-15961				
	N	537446	RS1-15718				
	O	537446	RS1-15718				
	P	2059868	QQ1-15961				
	Q	537447	OV1-13043				
	R	837623	QZ1-11024				
	S	837623	QZ1-11024				
	T	537447	OV1-13043				
	U	2007891	RS1-12416				
	V	537447	RU1-19029				
	W	537447	RU1-19029				
	X	2007891	RS1-12416				

SIMC electrodes RS1-15718, RS1-12416, and RU1-19029 were new and had been used less than 3 times in sediment.

Both SABS electrodes were new.

Appendix C. Number of calibration standards (5 vs. 3-point): data tables

Calibration data: SIMC

Table C2. Calibration data for tests comparing 5 vs. 3-point calibration at SIMC. Values are measured electrode potentials (mV) in 5 or 3 calibration standards. "–" indicates calibration standards not used in 3-point calibrations.

Number of calibration standards	Replicate	Equip. ID	Calibration standard nominal sulfide concentration (µM)					Temp. (°C)
			100	500	1 000	5 000	10 000	
5	1	A	-856.3	-876.8	-885.8	-906.3	-914.5	22.2
5	2	C	-853.3	-875.5	-884.3	-904.7	-912.6	22.2
5	3	E	-856.3	-876.9	-885.5	-905.1	-912.8	21.5
5	4	G	-857.5	-876.5	-884.8	-904.6	-912.7	22.2
5	5	I	-857.1	-877.7	-886.1	-905.5	-912.0	22.2
5	6	K	-855.5	-877.3	-886.1	-906.0	-914.0	22.1
5	7	M	-855.8	-877.1	-886.2	-906.4	-914.9	20.7
5	8	O	-859.7	-880.7	-889.1	-909.1	-916.3	21.5
5	9	Q	-854.9	-877.3	-885.9	-906.2	-914.4	20.8
5	10	S	-856.8	-877.9	-886.8	-906.4	-914.6	21.4
5	11	U	-853.6	-875.6	-883.8	-903.2	-910.9	23.1
5	12	W	-853.3	-875.5	-884.2	-903.8	-911.4	23.0
3	1	B	-856.4	–	-886.7	–	-914.5	22.2
3	2	D	-855.5	–	-884.7	–	-913.2	20.9
3	3	F	-852.1	–	-882.2	–	-910.3	22.6
3	4	H	-853.4	–	-882.1	–	-910.3	22.8
3	5	J	-855.2	–	-885.7	–	-913.7	22.3
3	6	L	-855.5	–	-885.5	–	-913.6	22.6
3	7	N	-860.4	–	-889.4	–	-917.7	20.4
3	8	P	-855.8	–	-884.7	–	-912.9	21.3
3	9	R	-856.5	–	-886.9	–	-915.1	21.3
3	10	T	-854.3	–	-885.1	–	-913.7	22.3
3	11	V	-852.7	–	-882.0	–	-909.8	23.6
3	12	X	-852.0	–	-881.0	–	-908.8	23.6

Appendix C. Number of calibration standards (5 vs. 3-point): data tables

Calibration data: SABS

Table C3. Calibration data for tests comparing 5 vs. 3-point calibration at SABS. Values are measured electrode potentials (mV) in 5 or 3 calibration standards. "–" indicates calibration standards not used in 3-point calibrations.

Number of calibration standards	Replicate	Equip. ID	Calibration standard nominal sulfide concentration (μM)					Temp. (°C)
			100	500	1 000	5 000	10 000	
5	1	1	-852.8	-875.3	-884.1	-904.6	-913.3	21.0
5	2	1	-852.2	-874.6	-883.6	-904.2	-912.7	21.0
5	3	1	-852.1	-874.3	-883.1	-903.8	-912.2	21.0
5	4	2	-855.9	-877.1	-885.5	-905.9	-914.2	21.0
5	5	2	-853.6	-876.8	-885.4	-905.9	-914.4	20.9
5	6	2	-853.6	-876.8	-885.3	-905.9	-914.2	21.5
5	7	1	-857.1	-878.6	-887.5	-908.2	-916.9	21.6
5	8	1	-856.8	-878.3	-886.9	-907.5	-915.9	21.6
5	9	1	-857.0	-878.9	-888.0	-908.9	-917.6	21.6
5	10	2	-849.6	-872.7	-882.3	-902.3	-911.5	21.5
5	11	2	-852.9	-873.8	-882.7	-903.4	-912.7	21.5
5	12	2	-851.8	-873.9	-883.2	-902.9	-911.4	21.5
3	1	2	-851.9	–	-881.5	–	-910.6	21.1
3	2	2	-850.1	–	-882.1	–	-910.9	21.3
3	3	2	-850.9	–	-881.6	–	-910.7	21.3
3	4	1	-854.2	–	-885.9	–	-915.1	21.1
3	5	1	-853.0	–	-884.9	–	-913.8	21.3
3	6	1	-854.5	–	-885.2	–	-914.4	21.3
3	7	2	-854.0	–	-884.0	–	-912.7	21.5
3	8	2	-853.1	–	-884.3	–	-913.6	21.5
3	9	2	-853.4	–	-885.0	–	-914.4	21.5
3	10	1	-856.8	–	-887.6	–	-917.2	21.6
3	11	1	-856.4	–	-888.1	–	-917.5	21.5
3	12	1	-855.5	–	-887.9	–	-917.6	21.6

Appendix C. Number of calibration standards (5 vs. 3-point): data tables

Test data: SIMC

Table C4. Results from tests comparing 5 vs. 3-point calibration at SIMC. Values are sulfide concentrations (µM) and electrode potentials (mV) measured in 4 test solutions.

Number of calibration standards	Replicate	Equip. ID	Test solution nominal sulfide concentration (µM)							
			250		750		2 500		7 500	
			µM	mV	µM	mV	µM	mV	µM	mV
5	1	A	152	-862.3	574	-879.0	1 860	-894.0	5 530	-907.8
5	2	C	314	-869.1	777	-881.1	2 270	-894.7	6 450	-907.6
5	3	E	233	-867.1	642	-880.0	1 750	-892.3	5 330	-905.8
5	4	G	213	-866.4	659	-879.8	1 980	-893.1	5 880	-906.5
5	5	I	187	-865.1	534	-878.5	1 790	-893.0	5 220	-905.9
5	6	K	229	-866.7	674	-881.0	2 190	-895.9	7 130	-910.0
5	7	M	248	-867.8	678	-881.3	2 240	-896.5	6 650	-910.0
5	8	O	232	-870.7	707	-884.9	2 380	-899.9	7 560	-913.5
5	9	Q	253	-867.9	779	-882.8	2 240	-896.3	6 350	-909.1
5	10	S	246	-868.6	730	-882.8	2 520	-898.0	7 570	-911.3
5	11	U	222	-864.7	639	-878.8	2 180	-893.4	6 630	-906.7
5	12	W	224	-864.4	666	-879.1	2 350	-894.6	7 440	-908.1
3	1	B	231	-867.7	679	-881.9	2 230	-896.7	6 500	-909.6
3	2	D	291	-866.5	867	-879.9	2 940	-895.9	8 030	-908.8
3	3	F	242	-864.2	717	-878.1	2 280	-892.6	7 810	-907.4
3	4	H	214	-863.2	613	-876.3	1 860	-890.0	5 930	-904.2
3	5	J	261	-867.6	785	-882.2	2 870	-898.1	7 790	-911.1
3	6	L	247	-867.3	747	-881.7	2 500	-896.7	7 090	-909.4
3	7	N	241	-871.8	732	-885.6	2 510	-900.7	7 520	-914.3
3	8	P	244	-867.3	699	-881.7	2 290	-896.7	6 620	-909.4
3	9	R	253	-868.7	784	-883.7	2 340	-897.4	6 590	-910.1
3	10	T	262	-867.2	764	-881.8	2 430	-896.2	6 920	-909.2
3	11	V	259	-864.8	796	-879.1	2 740	-894.3	8 200	-907.5
3	12	X	206	-861.1	650	-875.5	2 280	-890.9	6 900	-904.5

Appendix C. Number of calibration standards (5 vs. 3-point): data tables

Test data: SABS

Table C5. Results from tests comparing 5 vs. 3-point calibration at SABS. Values are sulfide concentrations (µM) and electrode potentials (mV) measured in 4 test solutions. "–" indicates electrode potentials (mV) not recorded.

Number of calibration standards	Replicate	Equip. ID	Test solution nominal sulfide concentration (µM)							
			250		750		2 500		7 500	
			µM	mV	µM	mV	µM	mV	µM	mV
5	1	1	248	–	765	–	2 570	–	7 760	–
5	2	1	254	–	788	–	2 550	–	7 770	–
5	3	1	249	–	783	–	2 540	–	7 560	–
5	4	2	214	–	738	–	2 580	–	8 080	–
5	5	2	249	–	733	–	2 470	–	7 620	–
5	6	2	241	–	730	–	2 430	–	7 110	–
5	7	1	247	-869.1	761	-884.0	2 500	-899.2	7 570	-913.4
5	8	1	237	-868.2	730	-882.9	2 510	-898.7	7 870	-913.1
5	9	1	242	-868.8	732	-883.9	2 420	-899.5	7 270	-913.6
5	10	2	219	-866.2	690	-881.1	2 390	-896.3	7 220	-910.2
5	11	2	243	-866.0	713	-881.2	2 390	-896.3	7 220	-910.2
5	12	2	243	-866.3	722	-881.2	2 460	-896.7	7 470	-910.7
3	1	2	304	–	861	–	2 790	–	8 720	–
3	2	2	245	–	779	–	2 440	–	6 870	–
3	3	2	240	–	745	–	2 620	–	7 830	–
3	4	1	248	–	721	–	2 440	–	6 780	–
3	5	1	253	–	729	–	2 470	–	7 570	–
3	6	1	259	–	752	–	2 520	–	7 530	–
3	7	2	254	-866.1	806	-881.0	2 650	-896.2	8 190	-910.7
3	8	2	235	-864.8	801	-873.3	2 450	-895.6	7 360	-909.6
3	9	2	239	-865.2	732	-880.6	2 350	-895.9	7 370	-910.4
3	10	1	245	-868.7	742	-883.5	2 480	-899.3	7 500	-913.5
3	11	1	258	-869.3	764	-884.3	2 490	-899.7	7 430	-913.7
3	12	1	263	-869.0	753	-883.8	2 460	-899.4	7 450	-913.8

Appendix D. Standardized vs. non-standardized calibration: data tables

Equipment

Table D1. Meters and electrodes used in tests comparing standardized vs. non-standardized calibration.

Lab	Equipment ID	Meter	Sulfide Electrode	Lab	Equipment ID	Meter	Sulfide electrode
SIMC	A	2059868	QQ1-15961	SABS	1	2007890	Q01-13710
	B	2007891	OW2-10925		2	2042138	Q01-13706
	C	537447	OV1-16043				
	D	837623	QZ1-11024				
	E	491819	QO1-13714				
	F	537447	OV1-16043				
	G	837623	QZ1-11024				
	H	2059868	QQ1-15961				
	I	537447	QQ1-15961				
	J	491819	QO1-13714				
	K	2007891	OW2-10925				
	L	486278	QZ1-11182				

All SIMC electrodes were older (previously used in sediment).

Both SABS electrodes were new.

Appendix D. Standardized vs. non-standardized calibration: data tables

Calibration data

Table D2. Calibration data for tests comparing standardized (std) vs. non-standardized (non-std) calibration at SIMC. Values are measured electrode potentials (mV) in 5 calibration standards.

Calibration method	Replicate	Equip. ID	Calibration standard nominal sulfide concentration (µM)					Temp. (°C)
			100	500	1 000	5 000	10 000	
Std	1	A	-853.7	-874.7	-884.0	-903.7	-912.3	20.8
Std	2	C	-852.5	-874.8	-883.5	-903.3	-910.6	22.5
Std	3	E	-850.5	-872.3	-881.5	-901.3	-909.4	22.0
Std	4	G	-857.1	-879.1	-888.0	-908.1	-916.2	21.2
Std	5	I	-856.3	-877.3	-886.0	-905.6	-913.5	22.0
Std	6	K	-857.1	-878.0	-886.8	-906.7	-914.9	21.1
Non-std	1	B	-853.7	-875.1	-883.9	-903.9	-912.0	21.6
Non-std	2	D	-853.5	-875.1	-884.4	-904.1	-911.8	20.7
Non-std	3	F	-851.0	-873.6	-882.6	-902.7	-910.3	23.2
Non-std	4	H	-856.9	-876.6	-884.4	-904.6	-912.3	21.5
Non-std	5	J	-852.9	-873.8	-882.6	-902.1	-910.1	21.6
Non-std	6	L	-852.5	-873.4	-882.3	-902.3	-910.1	21.6

Table D3. Calibration data for tests comparing standardized (std) vs. non-standardized (non-std) calibration at SABS. Values are measured electrode potentials (mV) in 5 calibration standards.

Calibration method	Replicate	Equip. ID	Calibration standard nominal sulfide concentration (µM)					Temp. (°C)
			100	500	1 000	5 000	10 000	
Std	1	1	-855.6	-877.4	-886.4	-906.8	-915.5	21.5
Std	2	1	-858.4	-880.2	-888.9	-909.4	-918.2	21.6
Std	3	1	-857.3	-879.3	-888.2	-909.0	-917.6	21.6
Std	4	2	-854.6	-877.0	-885.7	-906.1	-914.2	21.5
Std	5	2	-854.6	-876.9	-885.8	-905.7	-914.4	21.6
Std	6	2	-853.4	-874.8	-883.7	-903.6	-913.4	21.8
Non-std	1	2	-854.1	-874.3	-883.3	-902.8	-911.3	21.5
Non-std	2	2	-852.5	-874.5	-883.5	-903.8	-912.2	21.5
Non-std	3	2	-853.0	-874.3	-882.9	-902.7	-911.7	21.6
Non-std	4	1	-865.5	-878.7	-887.4	-908.2	-917.1	21.5
Non-std	5	1	-854.2	-876.9	-885.9	-906.7	-915.7	21.6
Non-std	6	1	-854.9	-876.7	-885.4	-906.0	-914.6	21.8

Appendix D. Standardized vs. non-standardized calibration: data tables

Test data

Table D4. Results from tests comparing standardized (std) vs. non-standardized (non-std) calibration at SIMC. Values are sulfide concentrations (μM) and electrode potentials (mV) measured in 4 test solutions.

Calibration method	Replicate	Equip. ID	Test solution nominal sulfide concentration (μM)							
			250		750		2 500		7 500	
			μM	mV	μM	mV	μM	mV	μM	mV
Std	1	A	305	-868.6	808	-881.5	2 550	-895.8	7 330	-908.9
Std	2	C	231	-864.1	671	-878.5	2 290	-893.7	6 840	-906.6
Std	3	E	331	-866.7	816	-879.4	2 670	-893.5	7 870	-906.7
Std	4	G	233	-868.7	672	-882.9	2 110	-897.3	6 100	-910.4
Std	5	I	210	-865.8	582	-879.8	1 950	-893.7	7 480	-909.2
Std	6	K	246	-868.8	680	-881.9	2 250	-896.8	7 380	-911.3
Non-std	1	B	254	-865.9	815	-881.0	2 690	-895.9	7 670	-908.7
Non-std	2	D	280	-867.5	820	-881.9	2 690	-896.4	7 100	-908.0
Non-std	3	F	277	-865.2	806	-879.8	2 700	-895.0	7 890	-907.7
Non-std	4	H	253	-868.3	836	-882.7	2 630	-897.1	8 420	-910.6
Non-std	5	J	289	-866.7	783	-879.5	2 560	-894.0	9 170	-909.1
Non-std	6	L	283	-865.8	786	-879.1	2 620	-894.0	9 000	-909.0

Table D5. Results from tests comparing standardized (std) vs. non-standardized (non-std) calibration at SABS. Values are sulfide concentrations (μM) and electrode potentials (mV) measured in 4 test solutions.

Calibration method	Replicate	Equip. ID	Test solution nominal sulfide concentration (μM)							
			250		750		2 500		7 500	
			μM	mV	μM	mV	μM	mV	μM	mV
Std	1	1	255	-868.2	758	-882.8	2 580	-898.4	8 000	-912.6
Std	2	1	237	-869.9	699	-884.4	2 390	-900.0	7 180	-913.9
Std	3	1	246	-869.6	738	-884.2	2 450	-899.8	7 360	-913.8
Std	4	2	236	-866.4	721	-881.6	2 400	-896.7	7 220	-910.5
Std	5	2	243	-866.0	715	-881.2	2 440	-896.4	7 450	-910.4
Std	6	2	236	-864.6	755	-879.8	2 600	-895.2	7 760	-909.5
Non-std	1	2	244	-865.4	782	-880.2	2 760	-895.3	8 630	-909.5
Non-std	2	2	251	-865.4	760	-880.0	2 490	-895.1	7 340	-908.5
Non-std	3	2	251	-865.2	798	-879.9	2 820	-895.8	8 750	-909.6
Non-std	4	1	271	-870.1	800	-884.6	2 650	-900.0	7 980	-914.1
Non-std	5	1	290	-869.0	838	-883.6	2 760	-899.1	8 310	-913.3
Non-std	6	1	266	-867.9	817	-882.5	2 680	-897.7	8 250	-912.0

Appendix E. Degradation of standard solutions: data tables

Equipment

Table E1. Meters and electrodes used in tests measuring the degradation of sulfide standards over time.

Lab	Equipment ID	Meter	Sulfide Electrode	Lab	Equipment ID	Meter	Sulfide electrode
SIMC	A	537447	OV1-13043	SABS	1	2007890	Q01-13710
	B	491819	QO1-13714		2	2042138	Q01-13706
	C	2059868	QQ1-15961				
	D	486278	QZ1-11182				
	F	837623	QZ1-11024				
	G	537447	RU1-19029				

SIMC electrode RU1-19029 was new and had been used less than 3 times in sediment.

Both SABS electrodes were new.

Appendix E. Degradation of standard solutions: data tables

Calibration data: SIMC

Table E2. Calibration data for tests measuring the degradation of sulfide standards at SIMC. Values are measured electrode potentials (mV) in 5 calibration standards. Electrodes were recalibrated at each measurement time, in freshly prepared calibration standards. Time is the duration since the start of each replicate trial.

Replicate	Equip. ID	Time (h)	Calibration standard nominal sulfide concentration (µM)					Temp. (°C)
			100	500	1 000	5 000	10 000	
1	A	0	-855.4	-876.9	-885.7	-906.1	-914.6	22.2
		24	-855.6	-876.8	-885.6	-906.1	-914.6	21.8
		48	-854.1	-875.9	-885.0	-905.1	-913.1	23.8
		72	-853.6	-875.3	-883.8	-903.6	-911.6	22.0
		96	-853.4	-875.6	-884.2	-904.2	-912.5	20.9
2	B	0	-857.5	-877.5	-887.2	-907.3	-915.5	20.6
		24	-857.7	-878.4	-887.3	-907.4	-915.1	21.7
		48	-855.3	-876.7	-885.5	-904.7	-912.6	22.0
		72	-853.5	-875.4	-884.2	-905.1	-913.5	21.2
		96	-853.7	-875.5	-884.5	-904.2	-912.0	20.8
3	C	0	-855.6	-877.6	-886.4	-906.3	-914.5	23.2
		24	-856.7	-877.5	-885.6	-905.4	-913.7	22.0
		48	-856.4	-876.6	-885.7	-905.3	-913.4	21.5
		72	-855.9	-877.0	-885.7	-906.0	-914.2	22.4
		96	-856.2	-877.3	-885.5	-905.6	-913.8	20.6
4	D	0	-852.2	-872.0	-880.8	-900.7	-908.9	20.3
		24	-852.9	-874.8	-883.4	-902.7	-911.0	22.4
		48	-853.3	-874.8	-883.6	-903.5	-911.2	22.0
		72	-853.0	-875.2	-883.8	-904.0	-912.4	21.8
		96	-854.3	-874.6	-882.6	-902.5	-911.2	23.0
5	F	0	-855.3	-876.3	-884.6	-904.3	-911.8	20.7
		24	-855.2	-877.9	-886.4	-905.1	-912.8	20.2
		48	-855.5	-877.4	-885.8	-905.5	-912.5	21.1
		72	-855.3	-877.5	-885.9	-905.2	-912.7	21.4
		96	-855.6	-877.6	-886.2	-906.6	-915.0	20.5
6	G	0	-853.3	-874.7	-884.1	-904.0	-912.5	22.2
		24	-853.9	-875.3	-884.0	-903.8	-912.1	21.4
		48	-852.5	-874.4	-883.7	-903.6	-911.7	23.2
		72	-852.4	-874.3	-883.9	-903.2	-911.7	22.4
		96	-855.2	-875.5	-884.0	-903.3	-911.4	21.1

Appendix E. Degradation of standard solutions: data tables

Calibration data: SABS

Table E3. Calibration data for tests measuring the degradation of sulfide standards at SABS. Values are measured electrode potentials (mV) in 5 calibration standards. Electrodes were recalibrated at each measurement time, in freshly prepared calibration standards. Time is the duration since the start of each replicate trial. "–" indicates no data (there was a calibration error in trial 1K at 72 h, with the 10 000 µM standard).

Replicate	Equip. ID	Time (h)	Calibration standard nominal sulfide concentration (µM)					Temp. (°C)
			100	500	1 000	5 000	10 000	
1D	1	0	-857.2	-879.2	-888.2	-909.0	-917.8	21.6
		24	-856.4	-878.1	-887.1	-907.9	-916.6	21.5
		48	-856.6	-879.0	-888.0	-908.6	-917.2	21.5
		72	-856.6	-878.4	-887.3	-908.2	-916.9	21.5
		96	-854.6	-876.6	-885.5	-906.2	-915.2	21.5
1K	2	0	-853.8	-875.9	-884.6	-902.1	-913.7	21.6
		24	-854.0	-876.4	-885.6	-905.9	-914.6	21.5
		48	-855.1	-877.6	-886.6	-907.1	-916.0	21.5
		72	-854.3	-875.9	-884.4	-904.2	-	21.5
		96	-852.8	-875.1	-884.1	-904.1	-912.8	21.5
2D	1	0	-857.1	-879.3	-888.2	-908.8	-917.8	21.5
		24	-856.5	-879.0	-888.0	-908.6	-917.3	21.5
		48	-856.0	-877.9	-886.7	-907.7	-916.4	21.5
		72	-855.4	-876.9	-886.0	-906.8	-915.6	21.4
		96	-856.8	-879.4	-888.5	-909.2	-917.7	21.5
2K	2	0	-854.5	-876.9	-885.6	-905.9	-914.5	21.5
		24	-854.0	-876.9	-885.6	-905.5	-913.8	21.5
		48	-854.3	-875.0	-884.7	-905.5	-914.2	21.5
		72	-851.4	-875.5	-883.3	-903.7	-912.1	21.4
		96	-855.0	-877.4	-886.2	-906.2	-914.9	21.5
3D	1	0	-857.1	-879.3	-888.2	-908.8	-917.8	21.5
		24	-856.5	-879.0	-888.0	-908.6	-917.3	21.5
		48	-856.0	-877.9	-886.7	-907.7	-916.4	21.5
		72	-855.4	-876.9	-886.0	-906.8	-915.6	21.4
		96	-856.8	-879.4	-888.5	-909.2	-917.7	21.5
3K	2	Used same calibration as replicate 2K						

Appendix E. Degradation of standard solutions: data tables

Test data: SIMC

Table E4. Results from tests measuring the degradation of sulfide standards at SIMC. Values are sulfide concentrations (µM) and electrode potentials (mV) measured in 7 test standards. Time is the duration since the start of each replicate trial (when the test standards were prepared).

			Test standard nominal sulfide concentration (µM)													
	Equip.	Time	100		500		1 000		5 000		10 000		20 000		30 000	
Rep.	ID	(h)	µM	mV	µM	mV	µM	mV	µM	mV	µM	mV	µM	mV	µM	mV
1	A	0	102.0	-855.6	471	-876.1	939	-884.9	4 580	-905.0	9 290	-913.7	18 600	-922.6	28 400	-927.4
		24	86.5	-854.4	377	-873.2	694	-881.3	3 670	-902.5	7 090	-910.7	15 400	-920.2	26 100	-926.7
		48	77.9	-850.9	318	-868.9	540	-877.2	3 460	-900.8	7 130	-909.5	16 400	-919.1	28 500	-925.6
		72	55.2	-845.6	221	-864.3	457	-874.1	2 700	-896.0	5 740	-905.2	14 800	-916.1	26 400	-922.8
		96	51.3	-844.2	199	-862.9	321	-869.4	2 670	-896.3	6 010	-906.3	13 800	-916.4	24 400	-923.1
2	B	0	97.4	-856.9	534	-877.0	986	-886.5	4 950	-907.1	9 800	-915.3	21 000	-924.1	32 000	-928.0
		24	79.8	-854.8	369	-874.5	715	-883.0	4 260	-905.4	8 660	-913.5	19 800	-922.7	28 400	-926.7
		48	74.1	-851.6	307	-870.5	674	-880.4	3 990	-902.3	8 610	-911.3	18 800	-919.8	29 600	-925.2
		72	65.8	-848.1	270	-866.9	633	-878.5	3 880	-901.7	8 470	-911.8	17 800	-920.8	30 500	-926.9
		96	46.1	-843.5	181	-862.0	561	-877.3	3 280	-899.1	6 790	-908.2	15 500	-917.4	23 800	-922.2
3	C	0	101.0	-855.8	468	-876.7	932	-885.5	4 500	-905.1	9 350	-913.6	19 000	-922.2	29 300	-927.2
		24	83.2	-855.0	392	-872.4	680	-881.5	4 320	-903.9	8 480	-912.1	18 500	-921.3	29 600	-927.0
		48	87.3	-854.7	320	-870.9	668	-880.4	4 310	-903.2	8 360	-911.3	18 500	-920.6	28 400	-925.4
		72	101.0	-855.9	307	-870.7	625	-877.5	3 780	-902.4	9 750	-913.9	20 300	-922.7	28 300	-926.8
		96	99.3	-855.5	268	-868.7	546	-878.3	3 630	-901.9	8 310	-911.6	20 200	-921.8	27 900	-927.8
4	D	0	100.0	-852.2	498	-872.0	927	-878.9	4 770	-899.6	11 500	-909.8	19 900	-917.7	30 500	-922.9
		24	90.2	-851.5	354	-870.1	694	-879.3	4 340	-901.0	8 600	-909.3	17 600	-917.8	26 100	-922.5
		48	86.7	-851.3	329	-869.2	707	-879.2	3 450	-898.8	7 330	-907.7	18 300	-917.6	32 600	-924.6
		72	77.7	-849.8	310	-868.9	640	-878.6	3 940	-901.4	7 980	-910.0	16 800	-918.9	25 500	-923.9
		96	62.1	-848.3	292	-868.2	595	-876.5	3 430	-898.0	7 660	-907.8	18 600	-919.0	31 900	-925.7
5	F	0	89.2	-853.8	446	-874.9	902	-883.4	4 570	-903.2	10 000	-911.8	20 600	-919.6	31 700	-924.3
		24	87.4	-853.3	363	-873.4	699	-882.0	4 510	-904.0	8 740	-911.3	18 600	-919.6	27 700	-924.2
		48	63.3	-849.3	321	-871.4	667	-880.9	3 580	-901.4	6 470	-908.0	14 100	-916.0	20 400	-919.7
		72	62.9	-848.9	303	-870.6	620	-880.1	3 380	-900.5	6 600	-908.2	14 500	-916.6	17 700	-918.8
		96	62.8	-849.0	295	-870.4	617	-880.2	3 450	-901.9	5 750	-908.3	13 800	-918.9	16 700	-921.1
6	G	0	108.0	-854.0	519	-874.9	1 000	-884.1	5 040	-903.8	9 610	-912.3	19 200	-920.2	28 900	-925.2
		24	86.4	-852.3	379	-871.5	751	-880.5	4 720	-902.1	9 210	-911.1	18 910	-919.5	26 900	-924.2
		48	94.4	-852.0	352	-870.0	718	-879.5	4 540	-902.7	9 790	-911.7	17 300	-918.4	32 000	-925.1
		72	76.8	-848.1	290	-866.3	686	-878.0	3 730	-899.4	8 920	-909.8	16 800	-917.3	31 000	-925.5
		96	39.5	-843.5	219	-865.1	488	-875.1	3 320	-898.3	7 480	-908.1	17 600	-918.1	30 900	-925.1

Appendix E. Degradation of standard solutions: data tables

Test data: SABS

Table E5. Results from tests measuring the degradation of sulfide standards at SABS. Values are sulfide concentrations (µM) and electrode potentials (mV) measured in 7 test standards. Time is the duration since the start of each replicate trial (when the test standards were prepared). "–" indicates no data (due to calibration errors in replicate trial 1K at 72 h for test standards 10 000 - 30 000 µM).

			Test standard nominal sulfide concentration (µM)													
	Equip.	Time	100		500		1 000		5 000		10 000		20 000		30 000	
Rep.	ID	(h)	µM	mV	µM	mV	µM	mV	µM	mV	µM	mV	µM	mV	µM	mV
1D	1	0	90.2	-855.6	475	-878.4	970	-887.8	4 770	-908.5	9 770	-917.5	19 800	-926.4	30 100	-931.8
		24	54.8	-848.0	255	-869.0	680	-882.1	4 520	-906.6	9 530	-916.0	20 200	-925.3	30 300	-930.6
		48	23.9	-836.2	163	-863.2	566	-880.5	4 240	-906.5	9 080	-916.0	19 500	-925.5	30 200	-930.9
		72	34.8	-841.8	68	-851.1	468	-877.5	4 190	-905.9	8 800	-915.3	18 800	-924.8	28 900	-930.3
		96	1.5	-797.2	23	-834.2	396	-873.4	4 180	-904.0	8 710	-913.5	18 400	-923.1	28 300	-928.7
1K	2	0	89.6	-852.0	472	-874.7	976	-884.1	4 850	-904.4	9 770	-913.1	20 200	-922.1	31 200	-927.6
		24	56.6	-844.6	253	-866.6	648	-879.7	4 310	-903.6	9 170	-913.2	19 200	-922.5	29 400	-927.7
		48	22.2	-832.0	154	-860.8	549	-879.0	4 020	-904.6	8 490	-914.1	17 100	-923.0	26 900	-928.7
		72	37.8	-840.6	68	-848.8	468	-874.7	4 340	-902.5	–	–	–	–	–	–
		96	5.2	-813.6	27	-834.6	391	-871.8	4 060	-901.6	9 010	-911.5	19 100	-920.5	29 200	-926.0
2D	1	0	97.2	-856.5	486	-878.9	985	-887.9	4 960	-908.6	9 770	-917.4	19 400	-926.4	28 700	-931.4
		24	66.0	-850.7	347	-873.9	660	-882.6	4 280	-906.8	9 020	-916.0	18 600	-925.0	28 400	-930.4
		48	45.6	-845.0	254	-868.6	614	-880.5	4 350	-905.8	9 170	-915.2	19 100	-924.6	28 300	-929.6
		72	25.7	-836.5	220	-865.5	527	-877.4	4 390	-904.8	9 180	-914.2	19 200	-923.6	28 800	-928.7
		96	19.6	-833.5	147	-862.3	415	-876.6	3 990	-906.3	8 560	-915.6	18 400	-925.2	28 200	-930.3
2K	2	0	97.8	-853.8	486	-876.3	984	-885.1	4 920	-905.3	9 770	-913.8	19 400	-922.4	29 700	-927.6
		24	66.5	-848.1	342	-871.5	640	-879.9	4 350	-903.6	9 130	-912.6	19 500	-921.8	29 500	-926.9
		48	28.8	-836.4	241	-865.9	627	-878.7	4 210	-903.4	9 170	-913.1	18 200	-921.8	27 800	-927.3
		72	32.0	-835.1	220	-862.6	504	-874.8	4 300	-901.8	9 360	-911.3	19 700	-920.2	30 000	-925.3
		96	26.7	-836.7	144	-860.3	403	-874.4	4 090	-903.8	8 720	-913.1	18 300	-922.8	27 800	-927.5
3D	1	0	98.6	-856.6	475	-878.6	932	-887.3	4 620	-907.7	9 400	-917.0	18 500	-925.8	28 300	-931.3
		24	65.6	-850.6	321	-872.7	635	-882.2	4 150	-906.2	8 600	-915.4	17 700	-924.5	27 100	-929.8
		48	58.1	-848.4	266	-869.3	599	-880.1	4 290	-905.6	9 030	-915.0	18 300	-924.1	27 200	-929.1
		72	42.4	-843.4	195	-864.0	548	-877.8	4 420	-904.9	9 320	-914.4	19 200	-923.6	29 200	-929.0
		96	32.7	-840.7	141	-861.6	418	-876.9	4 020	-906.4	8 560	-915.6	18 400	-925.0	28 400	-930.5
3K	2	0	92.4	-851.3	459	-875.4	908	-884.1	4 620	-904.6	9 460	-913.5	19 700	-922.6	29 700	-927.6
		24	65.6	-848.1	306	-869.9	620	-879.6	4 180	-903.1	8 760	-912.2	19 400	-921.8	29 200	-926.8
		48	47.8	-844.0	258	-866.9	584	-877.8	3 870	-902.4	8 540	-912.3	17 400	-921.2	27 600	-927.1
		72	47.4	-840.5	197	-861.0	508	-874.9	4 140	-901.2	9 060	-910.9	19 700	-920.3	30 500	-925.6
		96	30.6	-838.1	130	-858.7	389	-873.5	3 830	-902.8	8 240	-912.4	17 600	-921.8	27 600	-927.4

Appendix F. Electrode accuracy post-calibration: data tables

Equipment

Table F1. Meters and electrodes used in tests measuring electrode accuracy post-calibration.

Lab	Equipment ID	Meter	Sulfide Electrode	Lab	Equipment ID	Meter	Sulfide electrode
SIMC	CA	486278	QZ1-11182	SABS	1	2007890	Q01-13710
	EA	537446	RS1-15718		2	2042138	Q01-13706
	CB	537447	OV1-13043		3	2131173	RS1-15720
	EB	491819	QO1-13714				
	CC	537446	RS1-15718				
	EC	491819	QO1-13714				
	CD	20078891	RS1-12416				
	ED	486278	QZ1-11182				
	CE	491819	QO1-13714				
	EE	537447	RU1-19029				
	CF	837623	QZ1-11182				
	EF	20078891	RS1-12416				

SIMC electrodes RS1-15718, RS1-12416, and RU1-19029 were new and had been used less than 3 times in sediment.

All SABS electrodes were new. SABS equipment combination 3 was used for controls only.

Appendix F. Electrode accuracy post-calibration: data tables

Calibration data: SIMC control electrodes

Table F2. Calibration data for tests measuring electrode accuracy post-calibration at SIMC: control electrodes. Values are measured electrode potentials (mV) in 5 calibration standards. Control electrodes were recalibrated at each measurement time. Time is the duration from the start of each replicate trial.

Rep.	Equip. ID	Time (h)	Calibration standard nominal sulfide concentration (µM) 100	500	1 000	5 000	10 000	Temp. (°C)	Rep.	Equip. ID	Time (h)	Calibration standard nominal sulfide concentration (µM) 100	500	1 000	5 000	10 000	Temp. (°C)
1	CA	0	-854.3	-875.8	-884.8	-905.1	-913.4	24.1	4	CD	0	-855.8	-877.2	-885.9	-906.2	-914.2	20.1
		1	-852.9	-874.8	-883.7	-903.7	-912.0	22.8			1	-856.1	-877.5	-886.0	-905.9	-914.2	20.4
		2	-854.5	-876.1	-884.5	-904.0	-911.8	23.4			2	-854.5	-876.1	-884.8	-905.1	-913.1	21.7
		3	-852.9	-874.5	-882.8	-902.2	-910.3	23.1			3	-855.1	-876.2	-884.6	-904.0	-912.7	20.9
		4	-853.0	-874.7	-883.3	-902.1	-909.2	23.8			4	-855.3	-876.3	-885.0	-904.3	-912.9	21.0
		12	-854.3	-876.1	-884.5	-903.7	-911.4	23.0			12	-855.1	-876.6	-885.3	-905.6	-913.8	21.5
		24	-853.0	-875.0	-883.5	-903.5	-911.6	21.5			24	-855.1	-876.1	-884.8	-904.6	-913.1	21.1
		48	-852.6	-874.7	-883.1	-901.2	-907.9	21.6			48	-853.8	-875.5	-884.0	-903.8	-911.7	21.6
		72	-852.2	-872.6	-880.8	-900.5	-908.2	20.9			72	-853.7	-874.9	-883.5	-903.8	-912.2	21.5
		96	-854.3	-876.7	-885.5	-905.5	-911.6	21.2			96	-854.1	-875.5	-884.2	-903.7	-911.0	21.3
2	CB	0	-855.5	-876.5	-885.0	-904.5	-911.6	22.2	5	CE	0	-853.3	-875.2	-883.9	-904.5	-913.0	20.9
		1	-855.1	-876.1	-884.2	-902.7	-910.5	22.4			1	-853.4	-875.3	-884.0	-904.6	-913.1	20.9
		2	-856.4	-877.0	-885.7	-905.1	-913.0	23.0			2	-853.3	-874.5	-883.1	-903.8	-912.3	21.8
		3	-853.9	-875.9	-884.8	-904.5	-911.8	22.3			3	-852.6	-874.4	-883.0	-902.6	-910.0	21.9
		4	-854.6	-876.3	-885.1	-904.6	-912.5	22.7			4	-855.3	-876.3	-885.0	-904.3	-912.9	21.0
		12	-854.8	-876.3	-885.0	-904.7	-912.2	23.0			12	-852.3	-873.0	-882.2	-902.4	-910.5	21.0
		24	-854.5	-875.9	-884.2	-903.9	-911.6	22.4			24	-851.6	-872.9	-881.5	-901.3	-909.9	21.0
		48	-854.2	-874.9	-883.4	-903.1	-910.7	21.9			48	-850.7	-872.6	-881.6	-901.8	-910.4	21.3
		72	-854.6	-874.4	-882.8	-902.2	-909.3	22.1			72	-852.0	-873.3	-882.2	-902.2	-910.7	20.5
		96	-853.2	-873.6	-882.3	-902.0	-909.4	21.8			96	-852.2	-873.9	-882.5	-902.8	-911.2	20.6
3	CC	0	-853.6	-876.5	-885.9	-905.8	-913.9	22.0	6	CF	0	-852.8	-875.1	-884.1	-904.3	-912.6	20.8
		1	-852.8	-875.1	-884.0	-904.4	-913.1	22.9			1	-852.6	-874.8	-883.9	-904.3	-912.6	21.0
		2	-853.9	-875.4	-884.5	-904.3	-912.5	22.9			2	-852.2	-874.6	-883.5	-903.1	-912.1	21.2
		3	-854.1	-875.7	-884.1	-904.1	-912.2	22.9			3	-852.1	-874.8	-883.7	-903.5	-912.0	21.5
		4	-853.5	-874.9	-883.7	-903.5	-911.7	22.8			4	-851.8	-874.2	-883.0	-903.2	-911.4	22.1
		12	-854.0	-876.4	-885.4	-905.7	-914.2	22.9			12	-852.3	-874.8	-883.4	-903.8	-912.1	22.0
		24	-852.6	-875.2	-884.3	-904.9	-912.9	22.8			24	-854.0	-876.7	-885.1	-905.1	-913.0	21.0
		48	-853.8	-876.4	-884.9	-905.0	-913.2	21.3			48	-854.1	-875.6	-884.4	-904.4	-912.6	20.4
		72	-853.5	-875.5	-884.5	-904.3	-912.6	20.9			72	-853.2	-875.6	-884.4	-904.5	-912.5	20.8
		96	-852.8	-873.7	-882.0	-902.0	-910.3	21.9			96	-853.3	-875.3	-883.7	-903.9	-911.8	20.3

Appendix F. Electrode accuracy post-calibration: data tables

Calibration data: SIMC experimental electrodes

Table F3. Calibration data for tests measuring electrode accuracy post-calibration at SIMC: experimental electrodes. Values are electrode potentials (mV) in 5 calibration standards. Experimental electrodes were calibrated once, at the start of each replicate trial.

Rep.	Equip. ID	Time (h)	Calibration standard nominal sulfide concentration (μM) 100	500	1 000	5 000	10 000	Temp. (°C)
1	EA	0	-860.4	-881.3	-890.2	-910.2	-917.7	23.9
2	EB	0	-857.9	-879.5	-887.9	-906.9	-914.3	22.6
3	EC	0	-853.8	-874.9	-884.4	-904.9	-914.0	22.8
4	ED	0	-850.6	-873.0	-882.0	-902.6	-910.1	20.6
5	EE	0	-854.8	-875.9	-883.5	-904.1	-911.9	21.9
6	EF	0	-854.8	-877.2	-886.1	-906.3	-914.5	21.6

Appendix F. Electrode accuracy post-calibration: data tables

Calibration data: SABS control electrodes

Table F4. Calibration data for tests measuring electrode accuracy post-calibration at SABS: control electrodes. There was no control electrode for replicates 1D and 1K. Values are measured electrode potentials (mV) in 5 calibration standards. Control electrodes were recalibrated at each measurement time, except at 1 and 3 h.

Rep.	Equip. ID	Time (h)	Calibration standard nominal sulfide concentration (µM) 100	500	1 000	5 000	10 000	Temp. (°C)
2D/2K	3	0	-857.5	-879.6	-888.8	-909.3	-918.0	21.5
		1	Used calibration for 0 h					
		2	-858.2	-879.6	-888.3	-908.6	-917.7	21.5
		3	Used calibration for 2 h					
		4	-856.7	-879.0	-888.3	-909.0	-917.4	21.5
		12	-855.2	-878.0	-887.3	-908.0	-916.8	21.5
		24	-855.1	-877.5	-886.5	-907.3	-916.1	21.5
		48	-856.5	-878.8	-887.7	-908.5	-917.1	21.5
		72	-854.5	-877.3	-886.6	-907.2	-916.2	21.5
		96	-854.2	-877.2	-885.9	-906.8	-915.0	21.5
3D/3K	3	0	-857.5	-879.6	-888.8	-909.3	-918.0	21.5
		1	Used calibration for 0 h					
		2	-858.2	-879.6	-888.3	-908.6	-917.7	21.5
		3	Used calibration for 2 h					
		4	-856.7	-879.0	-888.3	-909.0	-917.4	21.5
		12	-855.2	-878.0	-887.3	-908.0	-916.8	21.5
		24	-855.1	-877.5	-886.5	-907.3	-916.1	21.5
		48	-856.5	-878.8	-887.7	-908.5	-917.1	21.5
		72	-854.5	-877.3	-886.6	-907.2	-916.2	21.5
		96	-854.2	-877.2	-885.9	-906.8	-915.0	21.5

Appendix F. Electrode accuracy post-calibration: data tables

Calibration data: SABS experimental electrodes

Table F5. Calibration data for tests measuring electrode accuracy post-calibration at SABS: experimental electrodes. Values are measured electrode potentials (mV) in 5 calibration standards. Experimental electrodes were calibrated once, at the start of each replicate trial.

Rep.	Equip. ID	Time (h)	Calibration standard nominal sulfide concentration (µM) 100	500	1 000	5 000	10 000	Temp. (°C)
1D	1	0	-856.6	-879.7	-888.8	-909.4	-918.2	21.5
2D	1	0	-858.1	-880.4	-889.5	-910.1	-918.9	21.5
3D	1	0	-857.7	-879.8	-888.7	-909.0	-917.5	21.5
1K	2	0	-854.8	-876.9	-886.0	-905.8	-914.0	21.5
2K	2	0	-856.1	-878.3	-887.3	-907.7	-915.8	21.5
3K	2	0	-854.9	-877.1	-886.1	-906.3	-914.3	21.5

Appendix F. Electrode accuracy post-calibration: data tables

Test data: SIMC control electrodes

Table F6a. Results for control electrodes in tests measuring electrode accuracy post-calibration at SIMC: replicate trials 1, 2, and 3. Values are sulfide concentrations (μM) and electrode potentials (mV) measured in 5 test solutions. Control electrodes were recalibrated at each measurement time.

			Control test solution nominal sulfide concentration (μM)									
			100		500		1 000		5 000		10 000	
Rep.	Equip. ID	Time (h)	μM	mV	μM	mV	μM	mV	μM	mV	μM	mV
1	CA	0	97	-853.9	489	-875.5	985	-884.6	4 880	-904.8	9 430	-912.6
		1	111	-854.3	516	-875.2	1 020	-883.9	5 040	-903.8	10 100	-912.1
		2	102	-854.5	464	-875.0	898	-883.2	4 570	-902.9	10 000	-910.7
		3	103	-853.4	500	-874.5	1 010	-882.9	5 130	-902.5	10 300	-910.5
		4	106	-853.6	504	-874.7	992	-883.2	5 410	-902.9	10 400	-910.5
		12	99	-853.7	464	-874.9	936	-883.5	4 880	-903.1	9 830	-910.9
		24	108	-853.7	493	-874.5	984	-883.0	4 770	-902.6	9 430	-910.6
		48	112	-854.1	496	-874.6	960	-882.7	5 100	-901.4	11 900	-909.7
		72	104	-852.7	517	-872.9	1 010	-880.9	4 720	-899.8	9 820	-908.0
		96	110	-855.8	500	-876.7	939	-884.7	4 400	-903.9	10 700	-912.2
2	CB	0	101	-855.9	470	-876.0	922	-884.2	4 600	-903.8	7 370	-909.8
		1	100	-854.5	492	-875.5	1 010	-884.0	5 240	-903.0	10 300	-910.2
		2	91	-855.0	484	-876.3	948	-884.9	4 840	-904.5	9 660	-912.4
		3	124	-856.8	536	-876.7	1 060	-885.5	5 240	-904.9	11 000	-912.7
		4	108	-855.6	489	-876.1	910	-883.7	4 760	-904.1	9 830	-912.3
		12	103	-855.9	512	-876.8	976	-885.3	4 840	-904.6	10 600	-913.1
		24	94	-853.5	467	-874.9	925	-883.5	4 650	-903.2	9 990	-911.8
		48	102	-854.4	496	-874.7	960	-883.0	4 840	-902.7	9 820	-910.5
		72	104	-855.0	539	-875.3	1 090	-883.8	5 510	-903.2	11 700	-911.2
		96	100	-853.9	496	-874.2	984	-882.7	4 830	-902.2	11 100	-910.1
3	CC	0	118	-855.9	507	-876.7	943	-885.2	4 960	-905.7	10 100	-914.0
		1	103	-853.2	462	-874.1	911	-882.8	5 160	-904.8	9 610	-912.6
		2	104	-854.3	512	-875.7	963	-884.1	4 920	-904.1	9 870	-912.1
		3	100	-854.2	478	-875.1	952	-883.5	4 920	-903.9	10 000	-912.2
		4	109	-854.7	532	-875.7	1 050	-884.3	5 350	-904.5	10 500	-912.5
		12	118	-856.3	521	-877.3	1 040	-885.9	5 000	-905.8	9 600	-913.6
		24	126	-855.7	556	-876.6	1 020	-884.6	5 080	-905.2	10 400	-913.7
		48	110	-885.0	479	-875.8	968	-884.5	4 690	-904.2	9 430	-912.5
		72	112	-855.0	465	-874.6	920	-883.7	4 600	-903.7	9 820	-912.3
		96	104	-853.2	521	-874.2	983	-881.8	4 880	-901.8	10 400	-911.0

Appendix F. Electrode accuracy post-calibration: data tables

Test data: SIMC control electrodes

Table F6b. Results for control electrodes in tests measuring electrode accuracy post-calibration at SIMC: replicate trials 4, 5, and 6. Values are sulfide concentrations (μM) and electrode potentials (mV) measured in 5 test solutions. Control electrodes were recalibrated at each measurement time.

			Control test solution nominal sulfide concentration (μM)									
	Equip.	Time	100		500		1 000		5 000		10 000	
Rep.	ID	(h)	μM	mV	μM	mV	μM	mV	μM	mV	μM	mV
4	CD	0	102	-855.9	520	-877.4	1 070	-886.7	5 220	-906.6	10 600	-914.7
		1	98	-855.6	479	-876.8	945	-885.6	4 720	-905.1	9 890	-914.0
		2	104	-854.8	515	-875.9	1 080	-885.5	5 190	-905.4	10 200	-913.2
		3	97	-854.5	481	-875.9	1 000	-884.6	5 240	-904.2	9 920	-912.5
		4	94	-854.9	481	-876.0	978	-884.9	5 000	-904.3	10 100	-913.0
		12	101	-855.2	520	-876.7	1 030	-885.8	5 120	-905.5	10 400	-913.9
		24	99	-855.0	485	-875.9	959	-883.8	4 900	-904.4	9 750	-912.9
		48	92	-852.6	478	-874.8	945	-883.9	5 000	-903.8	10 400	-912.1
		72	105	-853.5	500	-875.0	1 030	-883.9	5 040	-903.5	10 300	-912.2
		96	94	-853.2	479	-874.7	944	-883.9	5 100	-903.9	10 600	-911.5
5	CE	0	101	-853.5	478	-874.7	947	-883.5	4 810	-904.0	9 680	-912.7
		1	99	-853.5	482	-874.8	931	-883.1	4 280	-902.7	8 920	-911.6
		2	99	-853.0	475	-874.3	1 020	-883.3	4 880	-903.4	9 370	-911.5
		3	96	-852.0	464	-873.4	891	-881.8	4 750	-902.0	9 820	-909.9
		4	89	-851.6	450	-873.3	982	-882.4	4 880	-902.1	9 220	-909.8
		12	102	-852.2	500	-873.1	977	-881.9	4 810	-902.2	10 100	-910.7
		24	93	-851.3	478	-872.5	968	-881.4	4 840	-901.2	8 990	-909.0
		48	116	-852.6	515	-873.0	992	-881.7	4 960	-901.7	9 230	-909.5
		72	97	-851.6	489	873.3	952	-881.6	4 840	-901.8	9 520	-910.0
		96	103	-852.6	475	-873.3	992	-882.3	4 840	-902.6	9 760	-911.1
6	CF	0	98	-852.4	474	-874.8	987	-883.2	4 840	-903.9	9 750	-912.3
		1	101	-852.7	496	-874.9	971	-883.8	4 920	-904.1	10 100	-912.8
		2	106	-853.0	496	-874.5	1 020	-883.7	5 350	-904.1	10 200	-912.5
		3	107	-853.1	493	-874.6	970	-883.4	4 880	-903.3	9 680	-911.7
		4	96	-851.2	504	-874.3	1 030	-883.3	5 000	-903.2	10 400	-911.9
		12	100	-852.4	482	-874.3	937	-882.5	4 590	-902.7	9 120	-911.0
		24	99	-853.9	456	-875.4	922	-884.2	4 610	-904.1	9 740	-912.7
		48	98	-853.5	489	-875.2	969	-883.7	4 850	-903.8	9 460	-912.1
		72	102	-853.6	489	-875.3	984	-884.2	4 840	-904.2	9 450	-912.3
		96	101	-853.5	468	-874.7	951	-883.1	4 770	-903.3	9 590	-911.6

Appendix F. Electrode accuracy post-calibration: data tables

Test data: SIMC experimental electrodes

Table F7a. Results for experimental electrodes in tests measuring electrode accuracy post-calibration at SIMC: replicate trials 1, 2, and 3. Values are sulfide concentrations (µM) and electrode potentials (mV) measured in 5 test solutions. Experimental electrodes were calibrated once, at the start of each replicate trial.

			Experimental test solution nominal sulfide concentration (µM)									
	Equip.	Time	100		500		1 000		5 000		10 000	
Rep.	ID	(h)	µM	mV	µM	mV	µM	mV	µM	mV	µM	mV
1	EA	0	106	-860.9	516	-881.4	1 030	-890.3	5 230	-910.5	11 200	-918.5
		1	104	-860.6	516	-881.3	1 040	-890.1	5 190	-910.2	11 200	-918.5
		2	101	-860.4	500	-881.0	969	-889.5	5 000	-909.8	10 400	-917.8
		3	86	-858.0	445	-879.5	883	-888.3	4 500	-908.5	9 390	-916.7
		4	84	-857.8	449	-879.5	879	-888.5	4 470	-908.3	9 050	-916.3
		12	95	-859.4	477	-880.4	947	-889.2	4 840	-909.4	10 400	-917.8
		24	96	-859.6	481	-880.5	925	-888.9	4 150	-907.6	8 490	-915.7
		48	96	-859.6	470	-880.2	897	-888.4	3 620	-905.8	6 950	-913.3
		72	92	-859.0	459	-879.9	883	-888.3	4 120	-907.4	7 080	-913.5
		96	93	-859.1	463	-880.0	862	-888.3	3 740	-906.2	7 610	-914.3
2	EB	0	103	-858.2	493	-879.3	976	-887.6	4 830	-906.5	8 940	-913.0
		1	99	-857.7	482	-879.0	960	-887.4	4 870	-906.5	9 630	-913.9
		2	101	-857.9	504	-879.6	1 000	-887.9	4 570	-905.9	11 000	-915.2
		3	99	-857.7	478	-878.9	952	-887.3	4 670	-906.1	10 300	-914.6
		4	91	-856.9	444	-877.9	862	-886.1	4 440	-905.5	9 630	-913.9
		12	94	-856.9	447	-878.0	876	-886.3	4 560	-905.8	10 000	-914.2
		24	94	-857.1	444	-877.8	876	-886.2	4 520	-905.7	9 540	-913.7
		48	87	-856.1	421	-877.2	814	-885.3	4 370	-905.3	8 280	-913.5
		72	86	-855.9	421	-877.2	862	-886.0	4 370	-905.3	9 810	-914.1
		96	88	-856.1	434	-877.6	876	-886.3	4 630	-906.0	10 000	-914.4
3	EC	0	116	-855.5	540	-875.7	1 020	-884.4	5 200	-905.0	10 300	-914.1
		1	102	-854.1	433	-872.8	950	-883.9	5 000	-904.5	9 710	-913.3
		2	103	-853.9	547	-875.8	1 000	-884.2	4 810	-904.1	9 480	-913.3
		3	97	-853.4	500	-875.0	978	-884.0	4 810	-904.1	9 420	-913.0
		4	102	-854.0	523	-875.6	985	-884.2	4 880	-904.8	9 270	-913.0
		12	96	-853.1	481	-874.5	936	-883.4	4 440	-903.3	8 720	-912.2
		24	96	-852.5	453	-873.7	876	-882.6	4 270	-902.9	7 900	-910.9
		48	85	-851.3	439	-873.0	825	-881.5	3 950	-901.6	7 270	-909.5
		72	88	-851.6	404	-871.8	790	-880.8	3 650	-900.9	6 890	-908.8
		96	78	-850.4	390	-871.7	739	-880.1	3 570	-900.1	7 050	-909.0

Appendix F. Electrode accuracy post-calibration: data tables

Test data: SIMC experimental electrodes

Table F7b. Results for experimental electrodes in tests measuring electrode accuracy post-calibration at SIMC: replicate trials 4, 5, and 6. Values are sulfide concentrations (µM) and electrode potentials (mV) measured in 5 test solutions. Experimental electrodes were calibrated once, at the start of each replicate trial.

			Experimental test solution nominal sulfide concentration (µM)									
	Equip.	Time	100		500		1 000		5 000		10 000	
Rep.	ID	(h)	µM	mV	µM	mV	µM	mV	µM	mV	µM	mV
4	ED	0	99	-850.5	493	-872.8	955	-881.6	4 590	-901.5	10 200	-910.3
		1	101	-850.9	486	-872.6	955	-881.4	4 080	-900.0	9 030	-909.0
		2	84	-848.2	415	-870.4	851	-879.9	4 180	-900.2	8 630	-908.5
		3	98	-850.3	475	-872.3	940	-881.3	4 310	-900.6	9 550	-909.6
		4	98	-850.6	472	-872.3	926	-881.1	4 620	-901.6	9 460	-909.5
		12	87	-848.9	475	-872.3	948	-881.3	4 660	-901.7	9 640	-909.7
		24	87	-848.5	449	-871.5	891	-880.5	4 450	-901.0	9 290	-909.3
		48	76	-846.6	421	-870.8	864	-880.2	4 240	-900.7	9 030	-909.0
		72	81	-847.6	424	-870.7	844	-879.8	4 150	-900.2	8 710	-908.6
		96	73	-846.2	403	-870.1	825	-879.5	4 110	-900.1	8 710	-908.6
5	EE	0	95	-853.8	442	-873.8	982	-883.4	4 920	-903.5	9 680	-910.4
		1	106	-855.4	476	-875.1	1 010	-883.3	4 960	-903.7	10 400	-912.2
		2	97	-854.0	467	-874.7	965	-883.0	4 850	-902.6	8 520	-910.1
		3	103	-854.0	454	-874.4	956	-882.9	4 550	-902.7	8 760	-910.3
		4	71	-850.0	391	-872.7	852	-881.8	4 240	-901.4	8 300	-909.8
		12	75	-850.7	371	-871.5	682	-879.0	3 300	-898.5	6 300	-906.4
		24	82	-851.9	403	-872.7	822	-881.0	3 860	-900.5	7 270	-908.0
		48	73	-850.1	354	-871.0	707	-879.4	3 380	-898.8	5 920	-905.8
		72	73	-850.4	394	-872.3	713	-879.5	3 250	-898.4	5 720	-905.3
		96	72	-850.2	376	-871.8	773	-880.5	3 460	-899.1	5 670	-905.1
6	EF	0	104	-855.8	489	-876.9	992	-886.0	4 890	-906.1	10 200	-914.8
		1	99	-854.2	469	-876.5	986	-885.4	4 800	-905.8	9 750	-914.3
		2	105	-855.5	504	-877.6	985	-885.9	4 890	-906.4	9 920	-914.4
		3	101	-855.1	496	-877.2	962	-885.2	4 650	-905.4	9 350	-913.6
		4	101	-855.0	489	-876.9	947	-885.6	4 470	-905.2	9 190	-913.6
		12	93	-853.6	469	-875.7	876	-884.4	4 440	-904.7	8 810	-913.1
		24	93	-853.5	437	-875.7	856	-884.3	4 260	-904.2	8 090	-912.3
		48	93	-853.7	459	-876.0	929	-885.1	4 470	-904.8	8 590	-912.7
		72	87	-852.9	428	-874.9	810	-883.7	4 130	-903.8	8 080	-911.9
		96	92	-853.5	412	-874.8	804	-883.6	3 840	-903.1	7 500	-910.4

Appendix F. Electrode accuracy post-calibration: data tables

Test data: SABS control electrodes

Table F8. Results for control electrodes in tests measuring electrode accuracy post-calibration at SABS. There was no control electrode for replicate trials 1D and 1K. Values are sulfide concentrations (µM) and electrode potentials (mV) measured in 5 test solutions. Control electrodes were recalibrated at each measurement time (except 1 and 3 h). Measurements for 100 and 5 000 µM test solutions in replicate trial 3K at 1 h (shown in bold italics) were at *c.* 20.5°C, while all other measurements were at 21.5°C.

			Control test solution nominal sulfide concentration (µM)									
	Equip.	Time	100		500		1 000		5 000		10 000	
Rep.	ID	(h)	µM	mV	µM	mV	µM	mV	µM	mV	µM	mV
2D	3	0	103	-858.0	504	-879.6	978	-888.5	4 920	-909.0	10 000	-918.0
		1	104	-858.1	500	-879.3	942	-888.0	4 730	-908.7	9 690	-917.6
		2	104	-858.5	508	-879.7	1020	-888.7	5 040	-908.7	9 690	-917.1
		3	98	-857.8	471	-878.8	969	-888.0	4 880	-908.5	9 610	-917.0
		4	99	-856.6	504	-879.2	993	-888.3	5 000	-909.0	10 300	-917.6
		12	99	-855.0	489	-877.7	971	-887.0	4 920	-907.8	9 770	-916.7
		24	97	-854.7	493	-877.4	1000	-886.4	4 920	-907.1	9 770	-915.8
		48	105	-857.3	508	-879.0	1030	-888.1	4 960	-908.3	9 680	-916.7
		72	111	-856.0	531	-878.0	1000	-886.5	5 000	-907.3	9 850	-916.1
		96	99	-854.6	486	-877.1	984	-886.5	4 920	-907.2	10 100	-915.5
3D	3	0	105	-857.6	516	-879.4	1 020	-888.3	4 960	-908.5	10 000	-917.2
		1	101	-857.2	504	-879.0	955	-887.4	4 770	-907.9	9 610	-916.8
		2	104	-856.6	496	-878.8	977	-887.7	4 740	-908.2	9 600	-916.8
		3	107	-857.1	500	-879.0	977	-887.7	4 810	-908.3	9 680	-917.0
		4	102	-857.0	486	-879.1	1 010	-888.0	4 770	-908.1	9 110	-916.6
		12	104	-856.1	496	-878.0	1 000	-887.0	4 960	-907.5	9 920	-916.2
		24	101	-856.4	493	-878.3	1 030	-887.2	5 160	-908.0	10 200	-916.6
		48	100	-854.6	500	-877.3	992	-886.1	4 960	-906.8	9 920	-915.6
		72	100	-854.7	504	-877.1	1 020	-885.8	5 160	-906.6	10 300	-915.7
		96	103	-856.3	512	-877.7	1 050	-886.8	5 120	-907.4	10 200	-916.5
2K	3	0	99	-857.8	475	-878.7	907	-887.6	4 410	-907.9	8 530	-915.8
		1	106	-855.3	489	-879.2	927	-887.8	4 380	-907.5	8 870	-916.5
		2	124	-858.1	572	-878.4	889	-887.0	4 510	-907.4	8 960	-916.1
		3	92	-856.8	450	-877.9	896	-886.0	4 510	-907.1	8 680	-915.1
		4	102	-857.3	486	-878.6	928	-887.4	4 480	-907.5	8 760	-916.0
		12	115	-857.3	511	-878.3	978	-886.9	4 740	-907.2	9 170	-915.8
		24	101	-855.3	486	-877.0	965	-885.9	4 630	-906.2	8 900	-914.7
		48	104	-857.0	472	-878.0	925	-886.7	4 450	-907.1	8 860	-915.6
		72	117	-856.8	511	-877.6	971	-866.3	4 730	-906.5	9 060	-915.0
		96	104	-854.7	473	-876.3	961	-885.4	4 490	-905.4	9 280	-914.3
3K	3	0	111	-858.4	508	-879.2	985	-887.8	4 880	-908.2	9 380	-916.3
		1	***131***	***-857.9***	486	-878.6	970	-887.5	***6 130***	***-907.9***	9 090	-916.0
		2	110	-857.6	493	-878.5	955	-887.4	4 630	-907.7	9 380	-916.5
		3	110	-857.6	493	-878.8	955	-887.3	4 520	-907.4	8 790	-915.7
		4	103	-857.2	462	-878.3	936	-887.1	4 450	-907.5	8 300	-915.2
		12	108	-856.7	500	-878.1	1 010	-887.1	4 770	-906.8	9 540	-916.2
		24	104	-856.9	489	-878.1	984	-886.7	4 850	-907.6	9 460	-916.4
		48	109	-856.3	508	-877.4	1 000	-886.1	4 740	-906.1	9 090	-914.1
		72	102	-855.2	508	-877.1	1 030	-886.0	5 160	-906.6	10 300	-915.5
		96	105	-856.4	508	-877.6	1 020	-886.5	4 700	-906.4	9 320	-915.1

Appendix F. Electrode accuracy post-calibration: data tables

Test data: SABS experimental electrodes

Table F9a. Results for experimental electrodes in tests measuring electrode accuracy post-calibration at SABS: replicate trials 1D, 1K, 2D, 2K. Values are sulfide concentrations (µM) and electrode potentials (mV) measured in 5 test solutions. Experimental electrodes were calibrated once, at the start of each replicate trial.

			Experimental test solution nominal sulfide concentration (µM)									
			100		500		1 000		5 000		10 000	
Rep.	Equip. ID	Time (h)	µM	mV	µM	mV	µM	mV	µM	mV	µM	mV
1D	1	0	105	-857.0	504	-879.6	971	-888.4	4 880	-909.2	9 920	-918.1
		1	104	-857.0	486	-879.1	978	-888.5	4 880	-909.1	9 770	-917.9
		2	96	-856.0	490	-879.2	956	-888.2	4 880	-909.1	9 690	-917.9
		3	87	-854.4	466	-878.4	928	-887.6	4 730	-908.7	9 770	-917.9
		4	87	-854.3	473	-878.7	928	-887.8	4 700	-908.8	9 320	-917.3
		12	96	-856.0	479	-878.9	921	-887.7	4 660	-908.4	9 320	-917.4
		24	97	-856.1	476	-878.8	928	-887.8	4 700	-908.6	9 320	-917.2
		48	95	-855.8	457	-878.2	881	-887.1	4 410	-907.8	8 750	-916.5
		72	97	-855.9	466	-878.4	901	-887.4	4 590	-908.2	9 100	-917.0
		96	91	-855.0	450	-877.9	874	-887.0	4 380	-907.6	8 680	-916.5
1K	2	0	99	-853.7	493	-876.5	977	-885.3	4 960	-905.4	9 680	-913.3
		1	99	-854.3	493	-876.4	970	-885.2	4 880	-905.1	10 200	-913.8
		2	96	-854.1	507	-877.1	970	-885.2	5 040	-905.6	10 100	-913.7
		3	82	-851.7	479	-876.0	948	-885.0	4 840	-905.0	10 000	-913.6
		4	93	-853.4	493	-876.4	955	-885.1	4 960	-905.6	10 000	-913.6
		12	93	-853.6	479	-876.0	920	-884.6	4 800	-905.0	9 510	-913.1
		24	83	-852.2	455	-875.3	892	-884.2	4 570	-904.4	9 430	-912.5
		48	85	-852.3	438	-874.8	846	-883.5	4 360	-903.8	9 120	-912.5
		72	86	-852.4	458	-875.3	872	-883.8	4 540	-904.3	9 510	-913.1
		96	79	-851.4	417	-874.1	820	-883.1	4 320	-903.6	8 520	-910.9
2D	1	0	101	-858.1	489	-880.1	970	-889.1	4 850	-909.7	9 690	-918.5
		1	101	-858.1	489	-880.1	963	-889.0	4 810	-909.4	9 610	-918.5
		2	101	-858.2	496	-880.3	977	-889.1	4 810	-909.7	9 770	-918.6
		3	95	-857.5	486	-880.0	948	-888.8	4 700	-909.4	9 390	-917.9
		4	98	-857.7	479	-879.8	941	-888.7	4 660	-909.2	9 320	-918.1
		12	92	-856.9	452	-879.0	892	-888.0	4 310	-908.2	8 410	-916.7
		24	81	-855.3	436	-878.5	859	-887.6	4 340	-908.2	8 410	-916.7
		48	86	-855.8	436	-878.5	839	-887.3	4 180	-907.8	8 210	-916.4
		72	77	-854.4	394	-877.1	760	-885.9	3 770	-906.6	7 470	-915.2
		96	78	-854.6	394	-877.1	796	-886.5	3 990	-907.2	7 650	-915.5
2K	2	0	102	-856.2	516	-878.5	985	-886.8	4 920	-907.1	9 920	-915.4
		1	107	-855.2	516	-878.3	1 020	-887.1	4 920	-907.1	10 200	-915.7
		2	95	-853.7	482	-877.4	950	-886.2	4 810	-906.7	10 000	-915.4
		3	98	-855.5	472	-877.1	926	-886.0	4 550	-906.1	9 280	-914.7
		4	101	-855.8	486	-877.5	985	-886.7	4 890	-906.8	9 840	-915.2
		12	94	-855.1	472	-877.2	933	-886.1	4 590	-906.7	9 040	-914.3
		24	83	-853.3	408	-875.2	806	-884.2	4 010	-904.5	8 100	-912.9
		48	94	-854.8	458	-876.8	898	-885.6	4 410	-905.6	9 040	-914.3
		72	84	-853.2	417	-875.5	819	-884.4	3 850	-904.1	8 030	-912.9
		96	80	-852.7	396	-874.6	758	-883.4	3 670	-903.3	7 020	-911.7

Appendix F. Electrode accuracy post-calibration: data tables

Test data: SABS experimental electrodes

Table F9b. Results for experimental electrodes in tests measuring electrode accuracy post-calibration at SABS: replicate trials 3D & 3K. Values are sulfide concentrations (µM) and electrode potentials (mV) measured in 5 test solutions. Experimental electrodes were calibrated once, at the start of each replicate trial.

			Experimental test solution nominal sulfide concentration (µM)									
			100		500		1 000		5 000		10 000	
Rep.	Equip. ID	Time (h)	µM	mV	µM	mV	µM	mV	µM	mV	µM	mV
3D	1	0	105	-858.3	504	-880.2	1 010	-888.8	5 000	-908.9	10 200	-917.7
		1	98	-857.2	486	-879.2	969	-888.1	4 880	-908.6	9 840	-917.3
		2	102	-857.7	496	-879.9	984	-888.4	4 880	-908.8	9 920	-917.3
		3	101	-857.7	496	-879.9	992	-888.6	5 040	-909.0	9 840	-917.2
		4	102	-857.9	504	-880.0	984	-888.5	5 040	-909.0	9 610	-917.1
		12	95	-857.0	462	-878.7	917	-887.5	4 470	-907.5	8 650	-915.7
		24	97	-857.2	479	-879.2	946	-888.1	4 920	-908.8	9 680	-917.1
		48	85	-855.2	448	-878.2	896	-887.1	4 440	-907.4	8 790	-915.9
		72	68	-852.2	348	-874.7	696	-884.0	3 530	-904.8	7 240	-913.5
		96	75	-853.8	388	-876.3	796	-885.7	3 940	-905.8	7 850	-914.5
3K	2	0	108	-856.0	516	-877.6	1 030	-886.6	5 130	-906.5	10 000	-914.2
		1	96	-854.3	493	-876.9	947	-885.3	4 690	-905.5	9 910	-914.3
		2	99	-854.7	489	-876.7	947	-885.4	4 690	-905.4	9 340	-913.6
		3	96	-854.4	472	-876.2	918	-885.0	4 440	-904.7	9 260	-913.3
		4	101	-854.5	486	-876.7	954	-885.4	4 690	-905.6	9 660	-914.0
		12	90	-853.4	452	-874.2	869	-884.1	4 100	-903.6	8 360	-912.3
		24	82	-852.1	426	-875.3	862	-888.3	4 510	-905.0	9 020	-913.1
		48	89	-853.3	420	-875.0	810	-883.3	3 870	-903.3	8 010	-911.9
		72	73	-850.6	396	-872.9	761	-882.5	3 690	-902.4	8 500	-912.4
		96	82	-852.2	402	-874.2	798	-883.1	3 910	-903.0	8 140	-912.0